ENVIRONMENTAL EVALUATION GROUP

AN EQUAL OPPORTUNITY / AFFIRMATIVE ACTION EMPLOY

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Some Models of Colloids Generation and Transport

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Providing an independent technical analysis of the Waste Isolation Pilot Plant (WIPP), a federal transuranic nuclear waste repository.

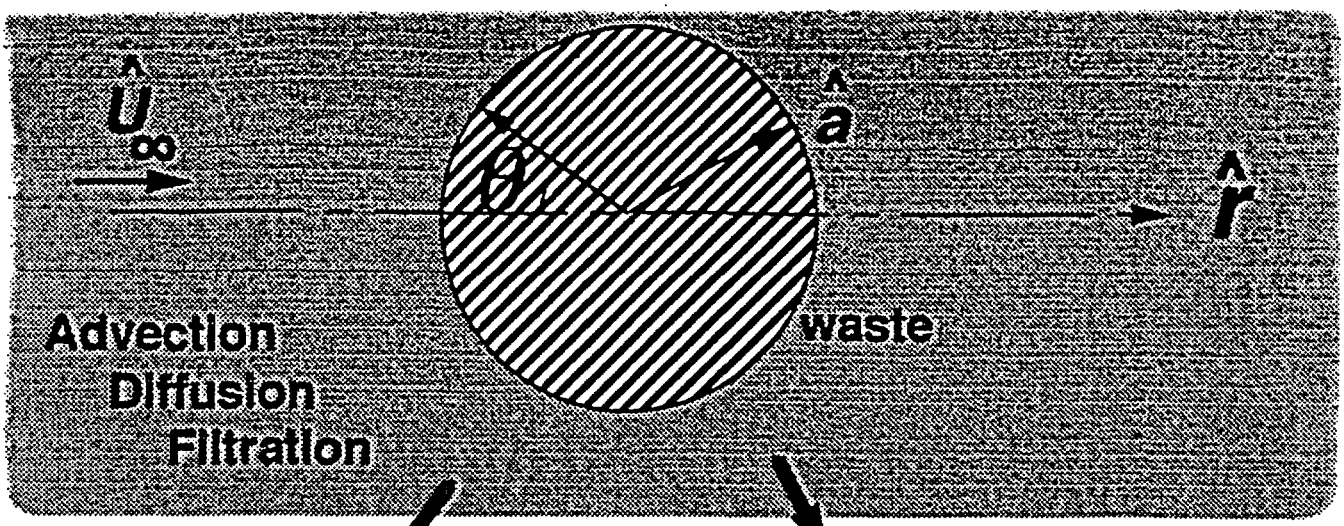
Definitions

Radiocolloid. Colloids of radioactive species. Probably formed from hydrolysis of actinides.

Natural colloids. Non-radioactive colloidal particles in natural waters.

Solute. Radioactive species in solution.

Pseudocolloids. Natural colloids which have sorbed radioactive solute.



in porous rock

- radiocolloid transport
  - advection
  - diffusion

in fractured rock

- radiocolloid transport
  - if colloids behave like particles, previously published solutions apply
    - new solutions if colloids interact with solute
- pseudocolloid transport
  - solutions for

	pseudocolloid	solute
advection	√	√
diffusion	√	√
sorption on		
fr. walls	√	√
fr. solids		√
matrix diff.		√
decay	√	√
filtration	√	

1. Fluid flow

The continuity equation for steady, incompressible flow around an infinite cylinder

$$\vec{\nabla} \cdot \vec{v}(\hat{r}, \theta) = 0, \tag{1}$$

where $\hat{r}$ is the radial coordinate [L],
θ is the angular coordinate [L], and
$\vec{v}(\hat{r}, \theta)$ is the vector of pore velocity symmetric over $\theta = \pi$.

The velocity vector can be decomposed into the radial and angular components

$$\vec{v} = -\hat{U}_\infty \cos\theta \left(1 - \frac{\hat{a}^2}{\hat{r}^2}\right) \vec{e}_r + \hat{U}_\infty \sin\theta \left(1 + \frac{\hat{a}^2}{\hat{r}^2}\right) \vec{e}_\theta,$$

$$\hat{r} \geq \hat{a}, 0 \leq \theta \leq \pi \tag{2}$$

2. Colloid concentration

The steady-state governing equation for colloid concentration in porous media is

$$\vec{\nabla} \cdot \vec{J}(\hat{r}, \theta) + \hat{S}(\hat{r}, \theta) = 0, \tag{3}$$

where

$$\vec{\nabla} = \vec{e}_r \frac{\partial}{\partial \hat{r}} + \vec{e}_\theta \frac{\partial}{\partial \theta} \tag{4}$$

and $\vec{J}(\hat{r}, \theta)$ is the colloidal mass flux [M/L^2-t],
$\hat{a}$ is the waste cylinder radius [L],
D_f is the diffusion coefficient of colloid in liquid [L^2/t],
$\vec{e}_r$ is the unit vector in the $\hat{r}$ direction,
$\vec{e}_\theta$ is the unit vector in the θ direction, and
$\hat{S}(\hat{r}, \theta)$ is the colloid filtration rate per unit volume of liquid per unit time [M/L^3-t].

The colloidal mass flux per unit area per unit time is defined as

$$\vec{J}(\hat{r},\theta) \equiv \vec{v}(\hat{r},\theta)\hat{C}(\hat{r},\theta) - D_f \left[\frac{\partial \hat{C}(\hat{r},\theta)}{\partial \hat{r}} \vec{e}_r + \frac{1}{\hat{r}} \frac{\partial \hat{C}(\hat{r},\theta)}{\partial \theta} \vec{e}_\theta \right], \tag{5}$$

We need to evaluate the filtration rate term $\hat{S}(\hat{r},\theta)$ in cylindrical geometry.

$$\hat{S}(\hat{r},\theta) = \Lambda \hat{U}_\infty \hat{C}(\hat{r},\theta) \sqrt{\left[\cos\theta \left(1 - \frac{\hat{a}^2}{\hat{r}^2}\right)\right]^2 + \left[\sin\theta \left(1 + \frac{\hat{a}^2}{\hat{r}^2}\right)\right]^2} \tag{6}$$

where Λ is a filtration coefficient for colloids, [1/L], to be determined.

We solve numerically for the radiocolloid flux from the waste.

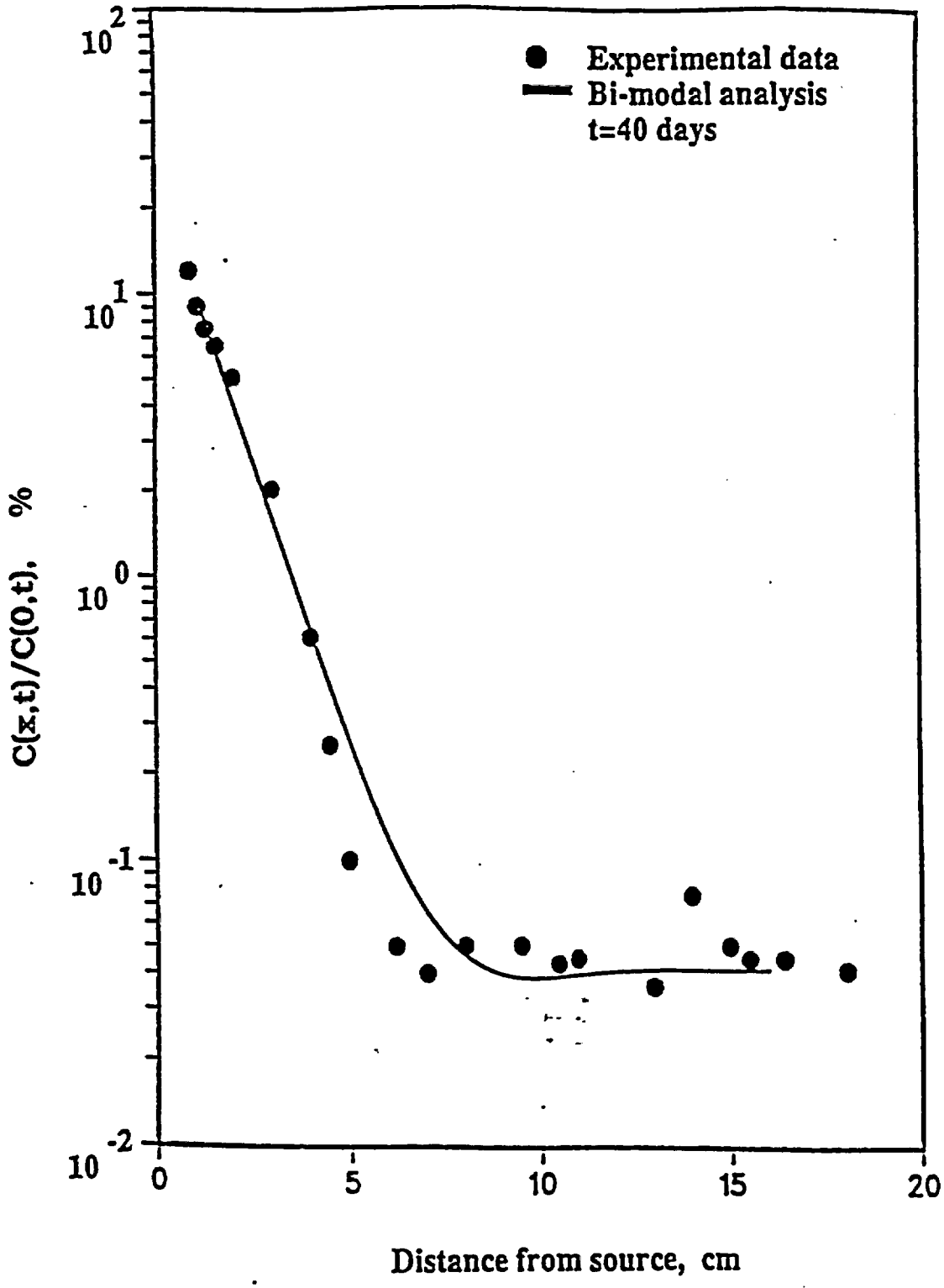
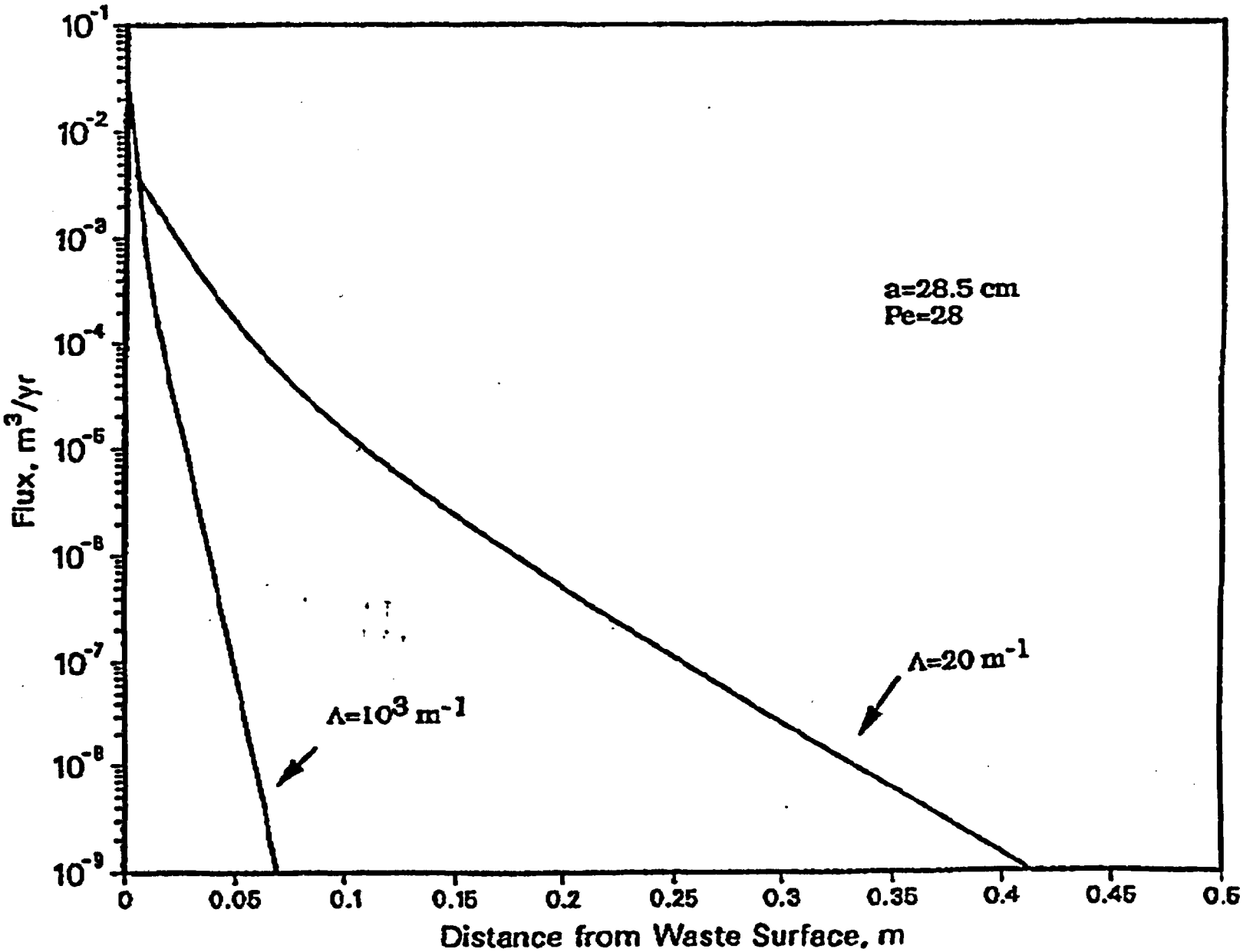
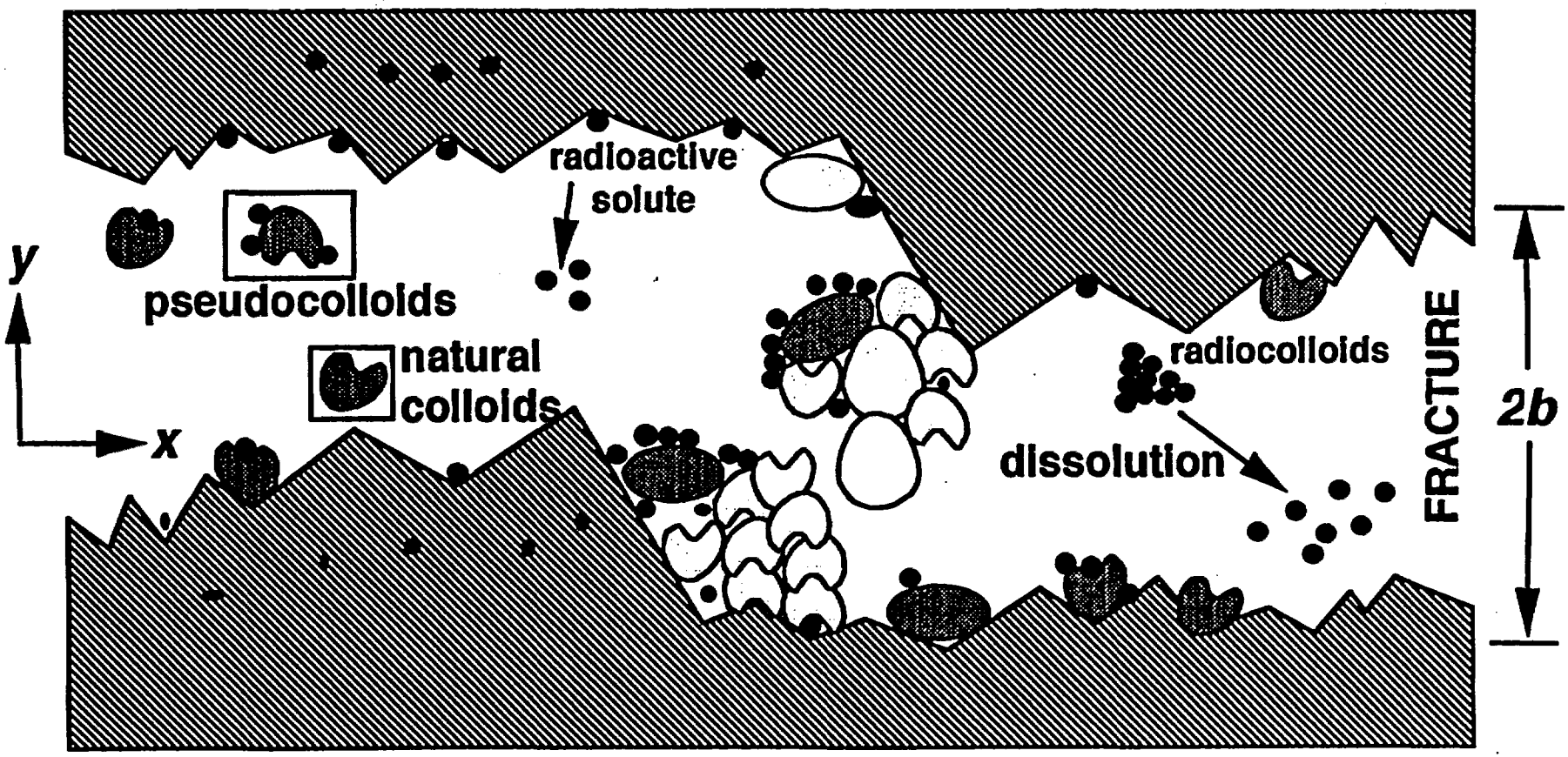


Figure 1. Normalized Neptunium Concentrations from the Experiment and Our Prediction Based on Bimodal Distribution of Filtration Coefficient as a Function of Distance Away from Inlet



Normalized radiocolloid Fluxes as a Function of Distance for Different Pore Velocities


radioactive
solute
pseudocolloids
natural
colloids
radiocolloids
dissolution
FRACTURE
2b
y
x

We consider one-dimensional advective-diffusive transport within the fracture, and assume that the colloids are too large to diffuse into the rock matrix. Neglecting the possible colloid filtration within a fracture, the governing equation of pseudocolloid migration in the fracture is

$$\epsilon_1\xi_1\frac{\partial c_1(x,t)}{\partial t}+\epsilon_1\xi_1 v_1\frac{\partial c_1(x,t)}{\partial x}+\epsilon_1 S_1(x,t)+\epsilon_1 S_2(x,t)-\epsilon_1\xi_1 D_1\frac{\partial^2 c_1(x,t)}{\partial x^2}+\epsilon_1\xi_1\lambda c_1=0,$$

$$x>0, t>0$$

where ϵ_1 is the ratio of liquid volume to total volume in the fracture [-],
$c_1(x,t)$ is the amount of species sorbed on the colloid per unit volume of solid colloid [M/L^3],
v_1 is the colloid pore velocity [L/t],
D_1 is the colloid dispersion coefficient [L/t],
λ is the decay constant [1/t],
ϵ_1 is the porosity within the fracture [-],
ξ_1 is the constant volume fraction of colloids in fracture liquid [-],
$\epsilon_1 S_1(x,t)$ is the rate of sorption to stationary solid [M/L^3 $-$ t],
and $\epsilon_1 S_2(x,t)$ is the rate of desorption from the pseudocolloid [M/L^3 $-$ t].

For the same species as solute in liquid in the fracture

$$\epsilon_1\frac{\partial c_2(x,t)}{\partial t}+\epsilon_1 v_2\frac{\partial c_2(x,t)}{\partial x}-\epsilon_1 S_2(x,t)+\epsilon_1 S_3(x,t)-\epsilon_1 D_2\frac{\partial^2 c_2(x,t)}{\partial x^2}+\epsilon_1\lambda c_2+\frac{q(x,t)}{b}=0, x>0, t>0$$

where
$c_2(x,t)$ is the solute concentration in the fracture liquid [M/L^3],
v_2 is the solute pore velocity [M/t],
$\epsilon_1 S_3(x,t)$ is the rate of solute sorption on stationary fracture solids [M/L^3 $-$ t],
b is the fracture half-width [L],

and $q(x,t)$ is the diffusive solute flux into the rock matrix [M/L^2-t], given by

$$q(x,t) = -\epsilon_p D_p \frac{\partial N(x,y,t)}{\partial y}\bigg|_{y=b}, \qquad x > 0, \qquad t > 0$$

where ϵ_p is the rock porosity [-],
D_p is the solute diffusion coefficient in water in porous rock [L^2/t],
and $N(x,y,t)$ is the solute concentration in pore water in the rock matrix [M/L^3].

For solute species sorbed on stationary fracture solids

$$(1-\epsilon_1)\frac{\partial c_3(x,t)}{\partial t} - \epsilon_1 S_3(x,t) + (1-\epsilon_1)\lambda c_3(x,t) = 0, \qquad x > 0, \qquad t > 0$$

where $c_3(x,t)$ is the concentration of sorbed solute species [M/L^3].

For pseudocolloids on the stationary fracture solids

$$(1-\epsilon_1)\xi_2\frac{\partial c_1(x,t)}{\partial t} - \epsilon_1 S_1(x,t) + (1-\epsilon_1)\xi_2\lambda c_1(x,t) = 0, \qquad x > 0, t > 0$$

where ξ_2 is the constant volume fraction of the sorbed colloid per unit volume of the stationary fracture solid [-].

Inside the rock matrix

$$R_p\frac{\partial N(x,t)}{\partial t} - D_p\frac{\partial^2 N(x,t)}{\partial y^2} + R_p\lambda N(x,t) = 0, \qquad x > 0, \qquad t > 0, \qquad y > 0$$

where R_p is the solute retardation coefficient in the rock matrix [-].

Linear sorption equilibrium between the solute species in the fracture liquid and the same species sorbed on the colloid is assumed. Both the solute species and the colloids in the fracture liquid are assumed to

undergo the linear sorption equilibrium with the fracture solids

$$K_{d_1} = \frac{\xi_2}{\xi_1}, \qquad [-]$$

$$K_{d_2} = \frac{c_3(x,t)}{c_2(x,t)}, \qquad [-]$$

$$K_{d_3} = \frac{c_1(x,t)}{c_2(x,t)}, \qquad [-]$$

Adding the above equations, an equation for c_1 is obtained in terms of an effective retardation factor R, an effective dispersion coefficient D, and the retarded velocity v.

$$R\frac{\partial c_1(x,t)}{\partial t} + v\frac{\partial c_1(x,t)}{\partial x} - D\frac{\partial^2 c_1(x,t)}{\partial x^2} + R\lambda c_1(x,t) + \frac{q(x,t)}{\epsilon_1 b} = 0, x > 0, t > 0 \qquad (*)$$

where

$$R = \left[\xi_1(1 + \frac{1-\epsilon_1}{\epsilon_1}K_{d_1})\right] + \left[1 + \frac{1-\epsilon_1}{\epsilon_1}K_{d_2}\right]\frac{1}{K_{d_3}}$$

$$v = v_1\left(\xi_1 + \frac{v_2}{K_{d_3}v_1}\right)$$

$$D = D_1\left(\xi_1 + \frac{D_2}{D_1K_{d_3}}\right)$$

Then the apparent migration front velocity of solute is

$$V = \frac{v}{R} = \frac{v_1\left(\xi_1 + \frac{v_2}{K_{d_3}v_1}\right)}{\left[\xi_1\left(1 + \frac{1-\epsilon_1}{\epsilon_1}K_{d_1}\right)\right] + \left[1 + \frac{1-\epsilon_1}{\epsilon_1}K_{d_2}\right]\frac{1}{K_{d_3}}}$$

where

$$\frac{dV}{dK_{d_3}} = A\left(\frac{v_1}{R_1} - \frac{v_2}{R-2}\right)K_{d_3}^2 > 0$$

$$A = \frac{R_1 R_2}{\left[\xi_1\left(1+\frac{1-\epsilon_1}{\epsilon_1}K_{d_1}\right) + \left(1+\frac{1-\epsilon_1}{\epsilon_1}K_{d_2}\right)\frac{1}{K_{d_3}}\right]^2}$$

Solving eq.(*) with the following initial and boundary conditions

$$N(x,\infty,t) = 0, \qquad x > 0, \quad t > 0$$

$$N(x,b,t) = \frac{1}{K_{d_3}}c_1(x,t), \qquad x > 0, \quad t > 0$$

$$N(x,y,0) = 0, \qquad x > 0, \quad y > 0$$

$$c_1(0,t) = K_{d_3}c_0, \qquad t > 0$$

$$c_1(\infty,t) = 0, \qquad t > 0$$

$$c_1(x,0) = 0, \qquad x > 0$$

where c_0 is the inlet solute concentration, we get the solution for the pseudocolloid concentration.

$$c_1 = \frac{2K_{d_3}c_o}{\sqrt{\pi}}\int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty} \exp\{f_1\}\,\mathrm{erfc}\,[f_2]\exp[f_3]\,d\eta \qquad x \geq 0, t \geq 0$$

where

$$f_1 = -\frac{\sqrt{v^2+4R\lambda D} - v}{2D}x$$

$$f_2 = \frac{x^2 \epsilon_p \sqrt{D_p R_p} K_{d_3}}{8Db\epsilon_1 \eta^2 \sqrt{t - \frac{Rx^2}{4D\eta^2}}}$$

$$f_3 = -\left(\eta - \frac{xv}{4D\eta}\right)^2$$

With FILTRATION, the first equation becomes

$$\epsilon_1 \xi_1 \frac{\partial c_1(x,t)}{\partial t} + \epsilon_1 \xi_1 v_1 \frac{\partial c_1(x,t)}{\partial x} + \epsilon_1 S_1(x,t) + \epsilon_1 S_2(x,t) - \epsilon_1 \xi_1 D_1 \frac{\partial^2 c_1(x,t)}{\partial x^2} + \epsilon_1 \xi_1 \lambda c_1 + \epsilon_1 \xi_1 v_1 \Lambda c_1 = 0,$$

$$x > 0, t > 0$$

where Λ is a filtration coefficient of radioactive solute sorbed on natural colloids inside the fracture, [1/L]. The solution for c_1 remains the same except for

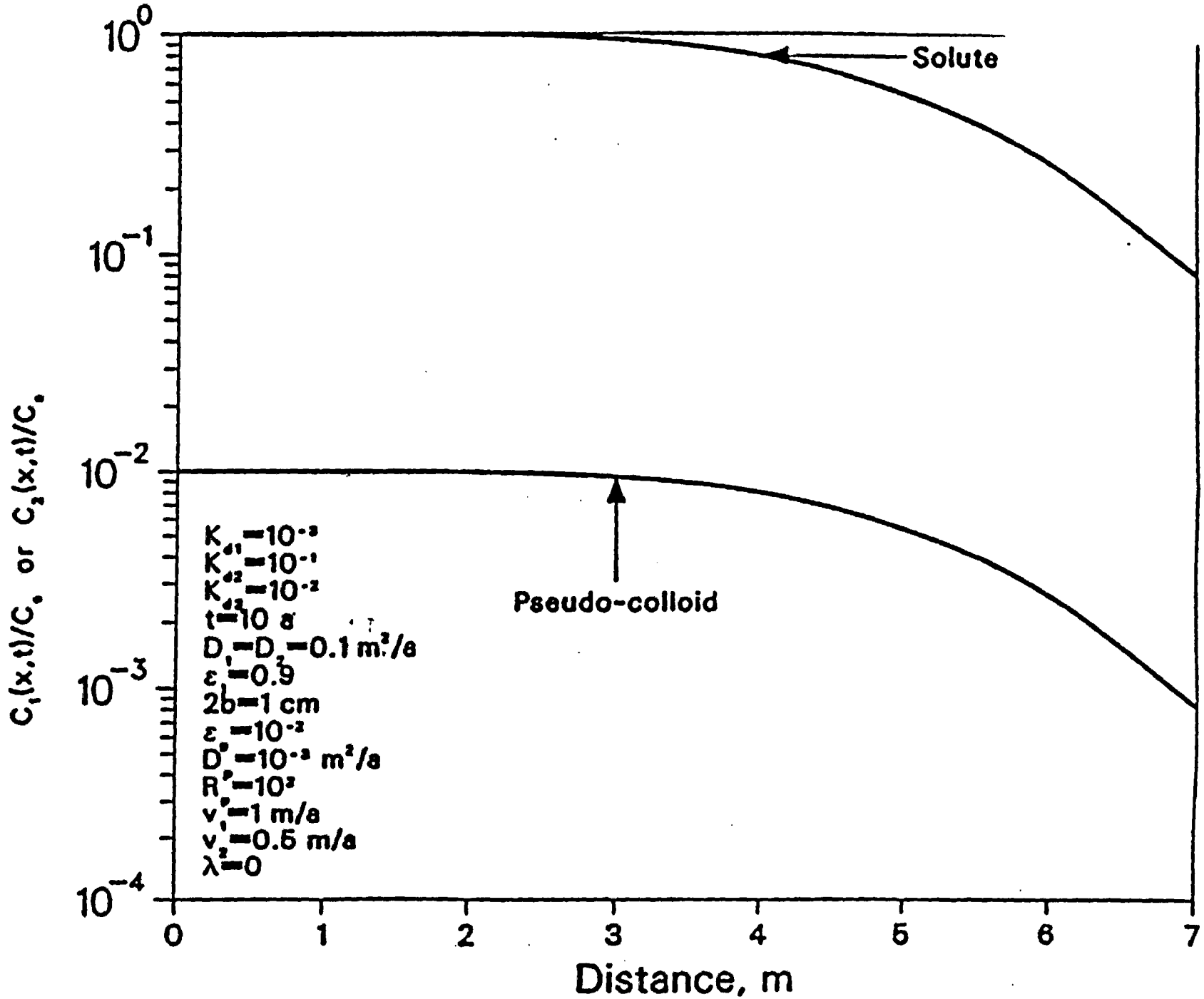
$$c_1 = \frac{2K_{d_3} c_0}{\sqrt{\pi}} \int_{\frac{x}{2}\sqrt{R/Dt}}^{\infty} \exp\left\{f_1^*\right\} \operatorname{erfc}\left[f_2\right] \exp\left[f_3\right] d\eta \qquad x \geq 0, \qquad t \geq 0$$

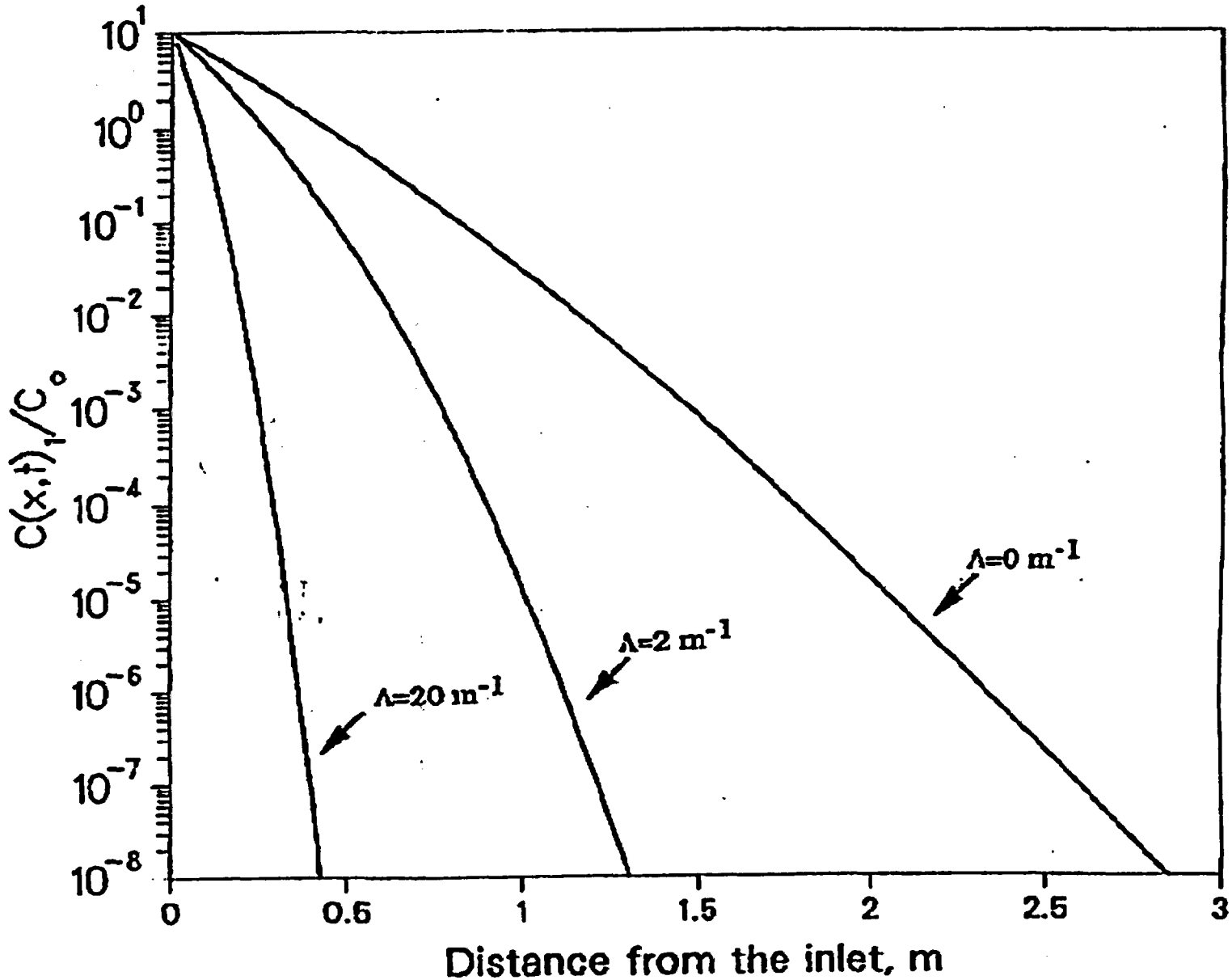
where

$$f_1^* = -\frac{\sqrt{v^2 + 4R^* D} - v}{2D} x$$

and

$$R^* = \left[\xi_1 \left(\lambda + \frac{1-\epsilon_1}{\epsilon_1} K_{d_1} \lambda + v_1 \Lambda\right)\right] + \left[1 + \frac{1-\epsilon_1}{\epsilon_1} K_{d_2}\right] \frac{\lambda}{K_{d_3}}$$


Solute
Pseudo-colloid
$K_{d1}=10^{-3}$
$K_{d2}=10^{-1}$
$K_{d3}=10^{-2}$
$t=10$ a
$D_1=D_2=0.1$ m²/a
$\varepsilon_1=0.9$
$2b=1$ cm
$\varepsilon_2=10^{-2}$
$D^p=10^{-3}$ m²/a
$R^p=10^2$
$v_1^p=1$ m/a
$v_2^p=0.5$ m/a
$\lambda^2=0$
$C_1(x,t)/C_o$ or $C_2(x,t)/C_o$
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0
1
2
3
4
5
6
7
Distance, m



~~Relative Concentration of Pseudo-colloid for Different Coefficients~~
with ~~Fracture Flow and Solute Matrix Diffusion~~

Where do we go from here?

We have developed some analytic means for predicting colloid generation and migration rates.

In so doing we have identified some parameters that need to be measured in laboratory and field studies:

filtration coefficients
sorption coefficients
diffusion coefficients

Do we know what these values are? Can they be measured? Can we bound the colloid problem if we have some idea of these values?

Is this an approach to performance assessment?

Is colloids a problem in radioactive waste disposal?

Greg Choppin, FSU

Natural Macromolecular Polyelectrolytes

(Humics,Fulvics)

A. Strong Complexors:

e.g., • 1 ppm; $UO_2Hu : UO_2^{2+} = 500-5000$

B. Colloid Formers:

as colloids themselves or as coatings on surfaces on mineral colloids

C. Strong Reductants:

quinone type structures have E ca. 0.7v

$PuO_2^{2+} = Pu(OH)_4$

D. Photolyze:

produce peroxide in surface waters, increases reduction strength

Metal – Humate Stability Constants

HA	pH	log β_1	Method	Analysis
Aldrich	6.0	6.27–0.04	LPAS	a
Gohy	6.0	6.68–0.47	UV Spec	a
Brad.	6.0	6.16–0.38	UV Spec	a
Brad.	6.0	6.53–0.30	Ultrafilt	a
Brad.	4.5	8.2–1.0	Sol Extr	b
Brad.	4.65	7.0–0.3	Spec	b

a: assumes Am binds to 3 $-CO_2^-$.

b: based on free $-CO_2^-$ groups per L. of solution.

Separation

a) J-13 well water acidified to pH 2 (w. HCl),

b) Passed through columns of XAD-8 macroporous resin at 3 - 6 gal/hr.,

c) Humics stripped with 0.1 M NaOH.

d) Eluant adjusted to pHa2 and passed through XAD-8, then stripped with 0.1 M NaOH, repeated twice more.

Separation (continued)

e) Almost 3000 gal. reduced 2.5 l after 3 columns.

f) Freezed dried, then purified by several cycles of dissolution in base, precipitation in acid with ultrafiltration.

g) Overall yield of 60 mg HA, 15 mg FA.

UV-VIS Absorbance

a) Humics characterized by ratio of absorbances at 465 and 665 nm (E_4/E_6 ratio.)

b) E_4/E_6 : 4 - 8 for humics.

c) E_4/E_6 : 4.1 for HA and 4.4 for FA from J-13.

Infrared Spectra

a) Spectra of HA and FA from J-13 similar to those of aquatic and lake sediments.

b) The spectra differ noticeable from HA spectra from soil samples.

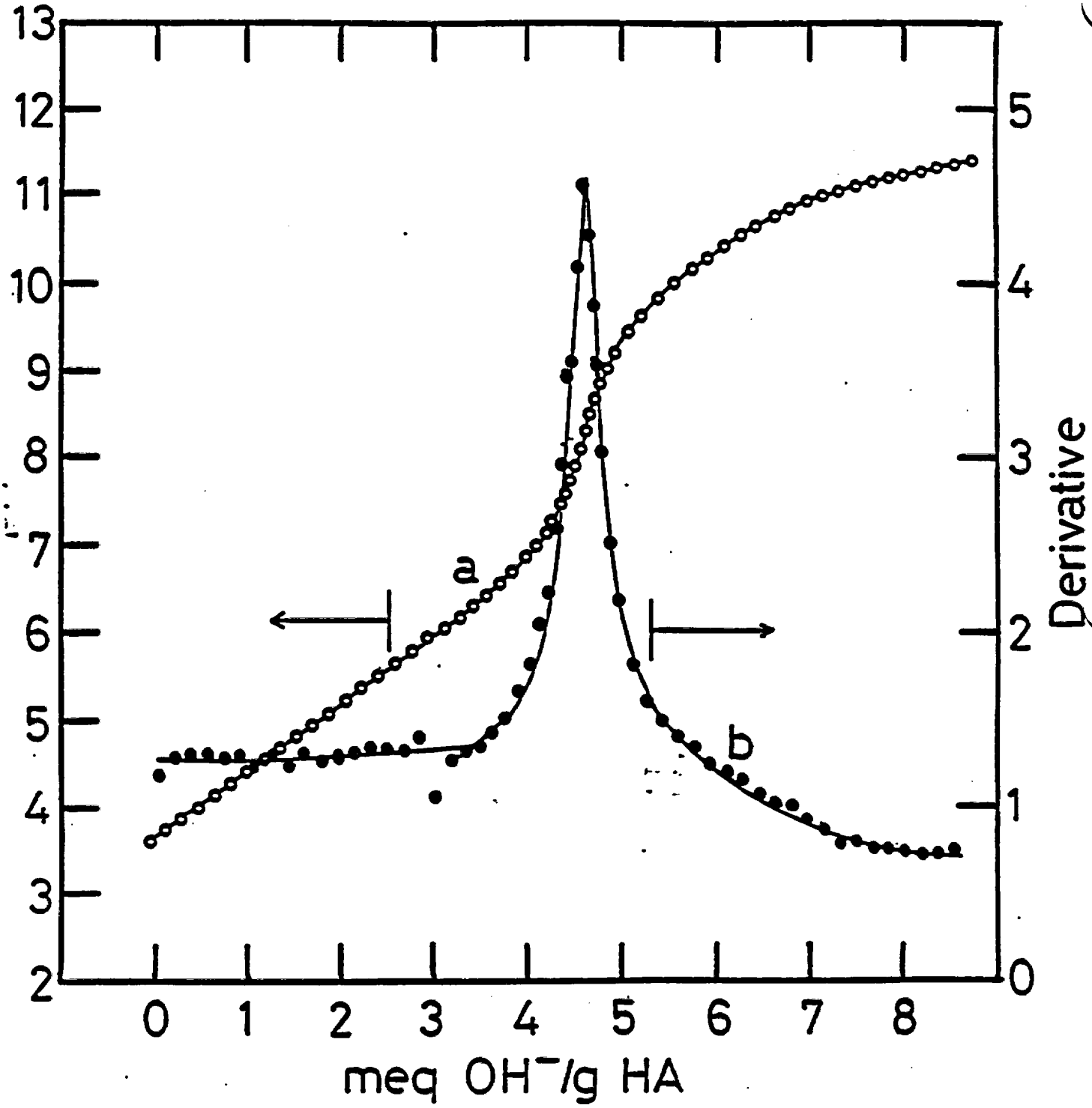
Other Properties

a) C-13 nmr - typical of low mole. wt. aquatic FA and HA.

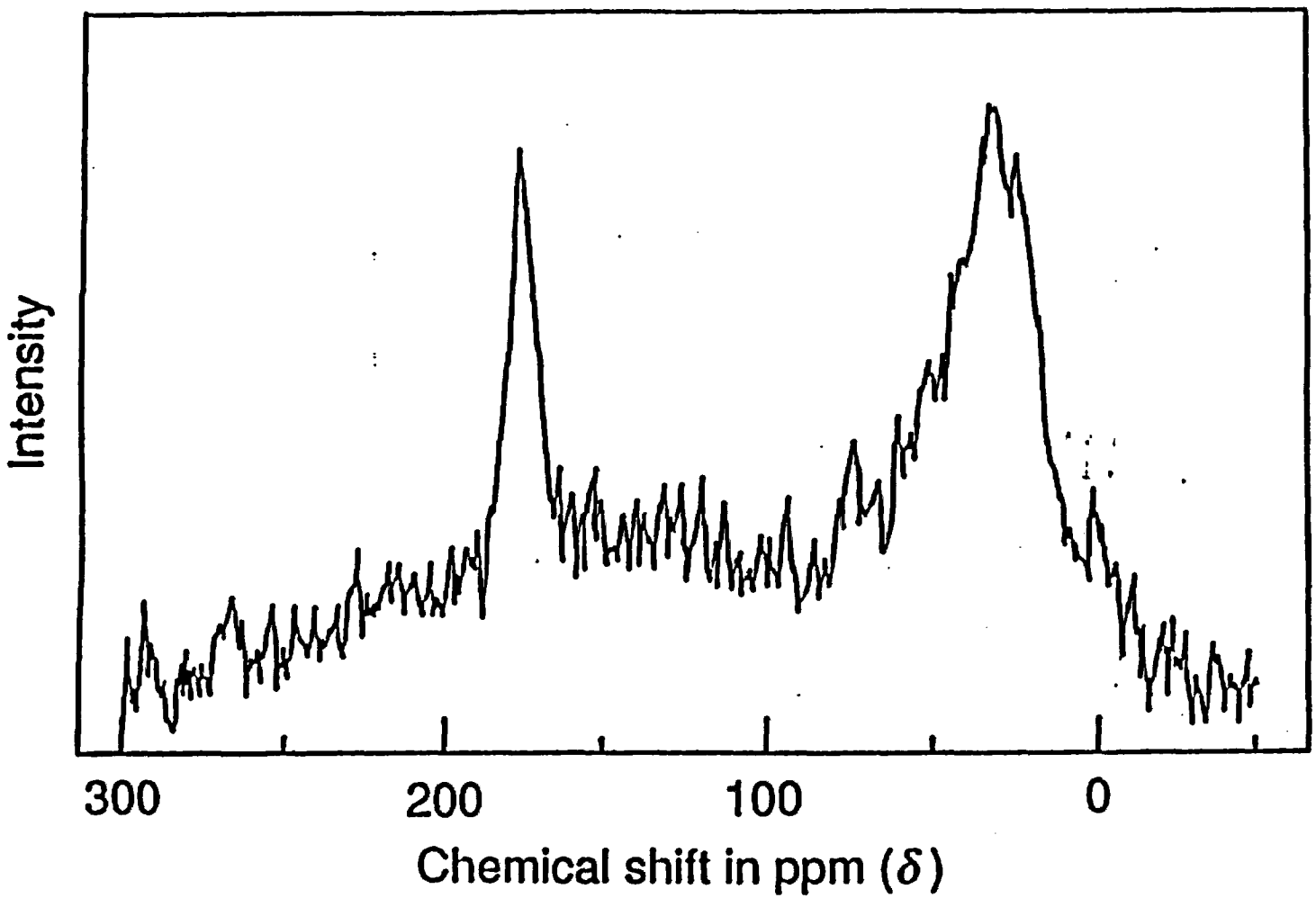
b) pH titration - 2.7 meq/g ($-CO_2H$)/g FA
- 4.6 meq/g ($-CO_2H$)/g FA

$$pKa(\alpha=0.5) = 4.6 \text{ FA}$$
$$= 5.6 \text{ HA}$$

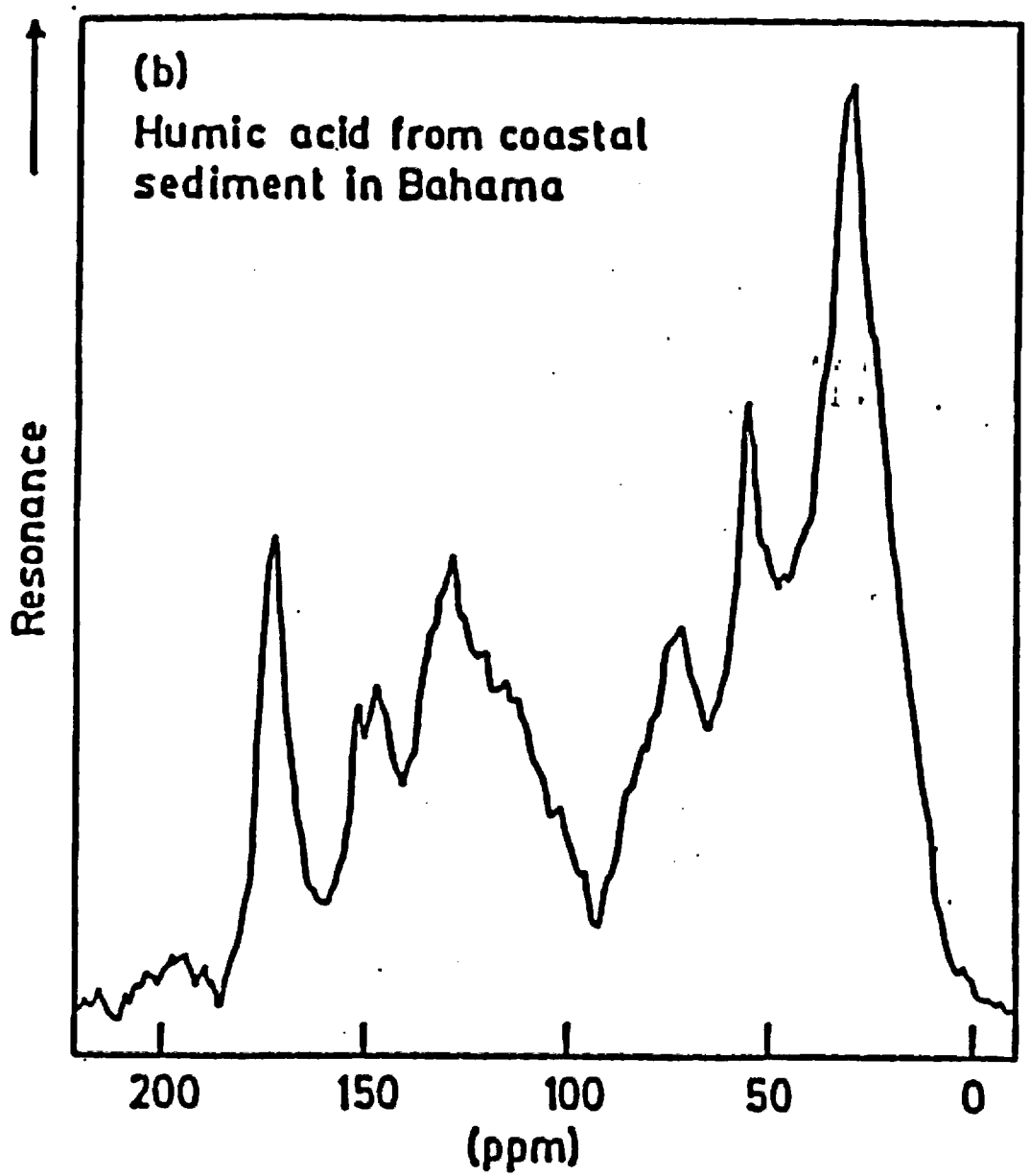
Properties are all typical of aquatic humics.



Titration and first derivative curves for J-13 water humic acid.



The CP/MAS C-13 NMR spectrum of the J-13 water humic acid.


(b)
Humic acid from coastal sediment in Bahama
Resonance
200
150
100
50
0
(ppm)

Binding Studies

a) Used solvent extraction method:

0.1 M ($NaClO_4$) + HDEHP in toluene

b) D vs [$-CO_2$] requires two parameters, β_1 and β_2.

$$\log \beta_1 = (7.57 \pm 1.43)\alpha + (4.47 \pm 0.49)$$
$$\log \beta_2 = (2.68 \pm 0.54)\alpha + (10.70 \pm 0.18)$$

Calculated Speciation

No Ca^{+2}

pH	Am	AmHu	$AmCo_3$	$Am(CO_3)_2$	Am(OH)
6.9	9.5e-5	1.0	1e-4	neg	2e-5
8.2	1.1e-4	1.0	3e-4	6e-5	4e-5

Corrected for Ca^{+2}

6.9	0.03	0.93	0.04	neg	0.005
8.2	0.02	0.41	o.43	0.09	0.05

Conclusions

Am(III) - HA could affect significantly.

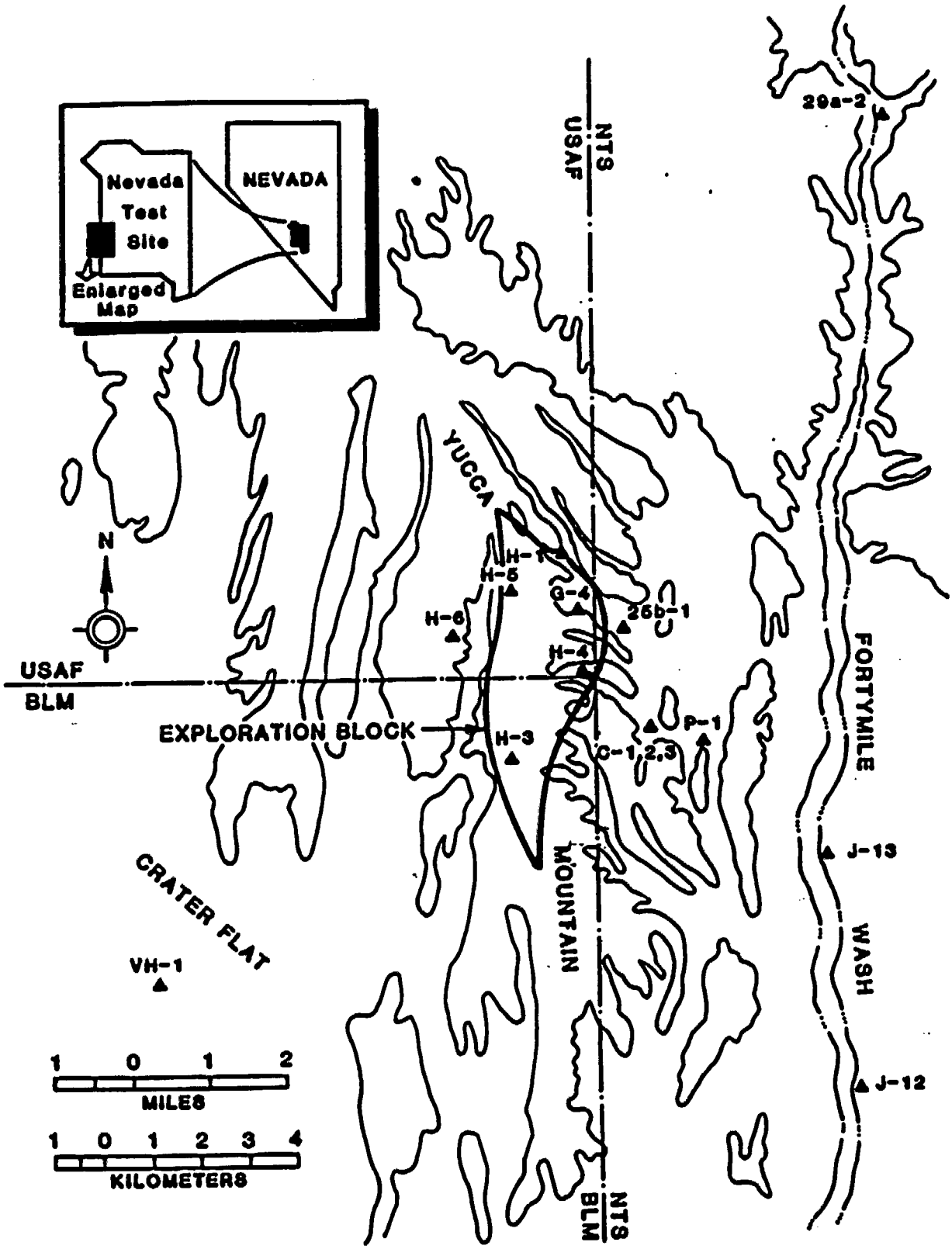
UO_2^{+2} - HA probably would not affect unless TOC > 0.2 ppm.

PuO_2^{+}, PuO_2^{+2} - would be reduced to Pu(IV) by HA.

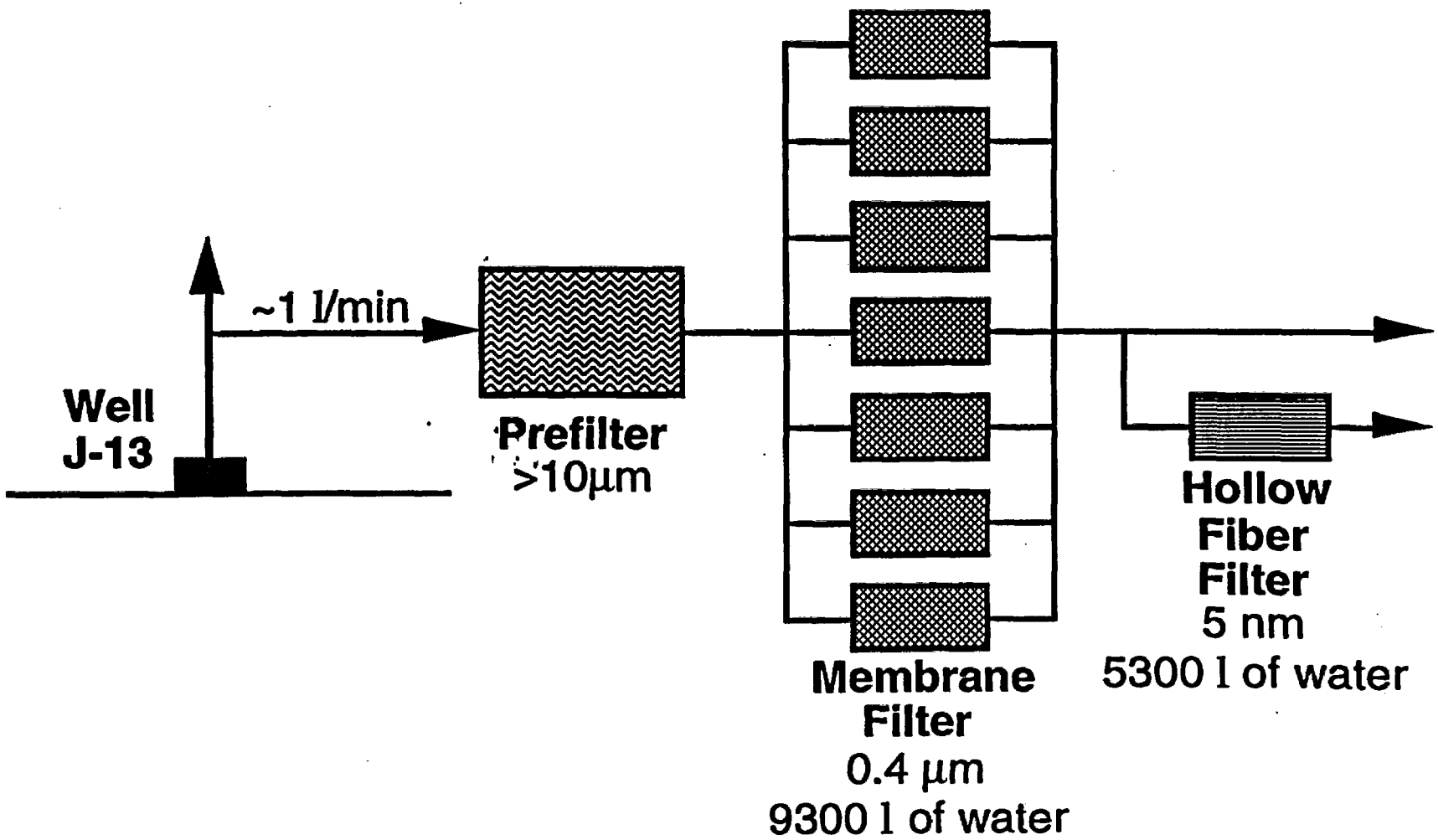
Particulate Material in Well J-13 Water

J. F. Kerrisk and A. Ogard

- Objective
  - Assess the potential for significant radionuclide transport on particulates in flowing groundwater
- Why Well J-13 water?
  - Established well (1963)
  - Routinely pumped
  - Close to Yucca Mountain
    - Topopah Spring Member
- Reference: LA-10929-MS


Nevada Test Site
NEVADA
Enlarged Map
N
USAF
BLM
EXPLORATION BLOCK
CRATER FLAT
VH-1
YUCCA
MOUNTAIN
NTS
USAF
NTS
BLM
H-1
H-5
H-6
H-4
H-3
G-4
25b-1
C-1,2,3
P-1
29a-2
J-13
J-12
FORTYMILE
WASH
1 0 1 2
MILES
1 0 1 2 3 4
KILOMETERS

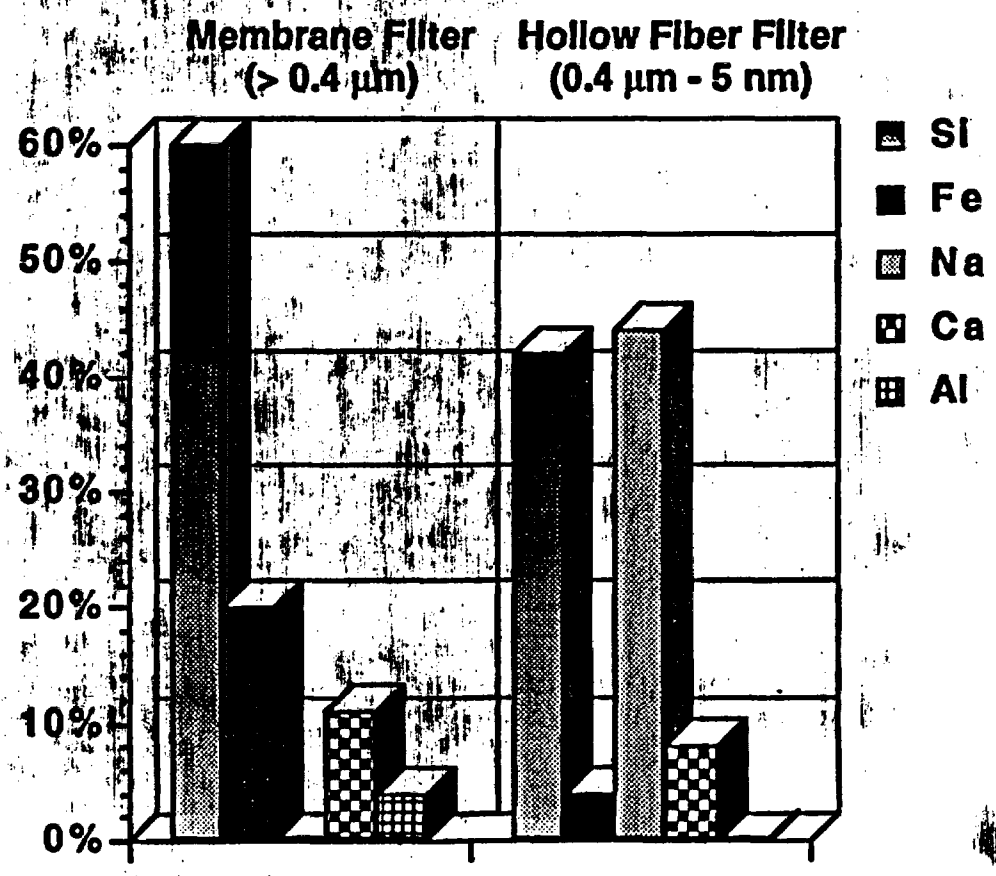
Sample Collection



Sample Analysis

- Membrane Filters (> 0.4 μm)
  - Water wash, centrifuge, alcohol wash, dry
  - Weigh
    - 0.25 g solid from 9300 l of water
    - 2.7×10^{-5} g solid/l water
  - Elemental analysis
- Hollow Fiber (0.4 μm - 5 nm)
  - Backflush
  - ~ 0.0025 g solid from 5300 l of water
  - Elemental analysis

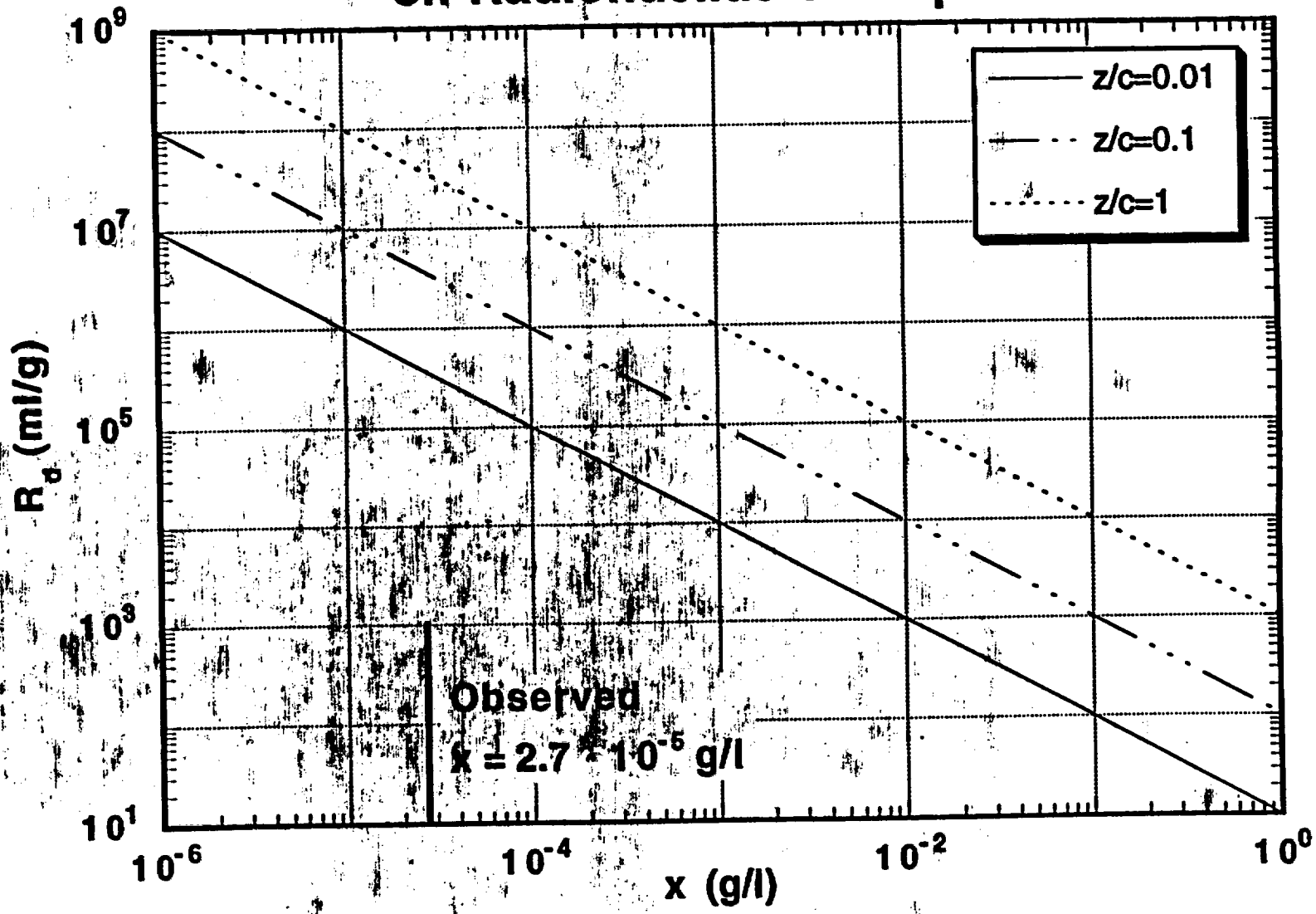
Cation Composition of Particulate Samples



Effect of Particulates in J-13 Water on Radionuclide Transport

- R_d is the sorption ratio of particulates in J-13 water (ml/g)
- x is the concentration of particulates in J-13 water (g/l)
- c is the dissolved radionuclide species concentration in J-13 water (moles/l)
- z is the moles of radionuclide sorbed on particulates/l water
  - $z = R_d \cdot c \cdot x/1000$
- z/c is the ratio of moles of radionuclide species sorbed on particulates/l water to moles of radionuclide species dissolved/l water
  - $z/c = R_d \cdot x/1000$

Effect of Particulates in J-13 Water on Radionuclide Transport



Conclusions/Questions

- If particulates in Well J-13 water are representative of groundwater under the repository and the sorption ratio of particulates is not significantly larger than repository material, radionuclide transport by particulates should not be a significant problem
- Is Well J-13 water representative of groundwater under the repository?
  - Reference: UCID-21867
- What is the sorption ratio of the particulate material?

Occurrence, Composition and Properties of Colloidal Particles at the NTS

Michael Whitbeck, DRI

Potential Significance of Colloids

- mobile binding sites competitive with fixed sites on rock matrix
- accelerated transport of contaminants via size exclusion

Double Layer Model

$$SOH_2^+ = SOH + H_o^+$$

$$K = (SOH)(H_o^+)/(SOH_2^+)$$

$$(H_o^+) = (H^+)\exp(-e\psi_o/kt)$$

physical properties emphasized

bulk electrolyte determines charge at surface, σ_o

dilute solutes not addressed

no surface complexation or 'ion pairs' (Yates)

assumes nonporous planar interface

Surface Complex Formation

$$[M^+]_\beta = [M^+]\exp(-e\psi_\beta/kt)$$

$$[SO\text{--}M] = K_M[SO^-][M^+]\exp(-e\psi_\beta/kt)$$

Validity of Model Assumptions

Surface physics?

Hard surfaced particles best

Surface chemistry ?

clean inorganic surfaces

OBJECTIVES

Collection of groundwater samples at 23 sites

Determination of mass abundance of colloids by size

Determination of composition of particles by size

METHODS

Pressure cell filtration at 20 psig: 1 - .03 micron

Size Exclusion Chromatography: 20-2 nm, 0.1M NaCl

Infrared Spectroscopy: 6x Beam Condenser

Mass Distribution

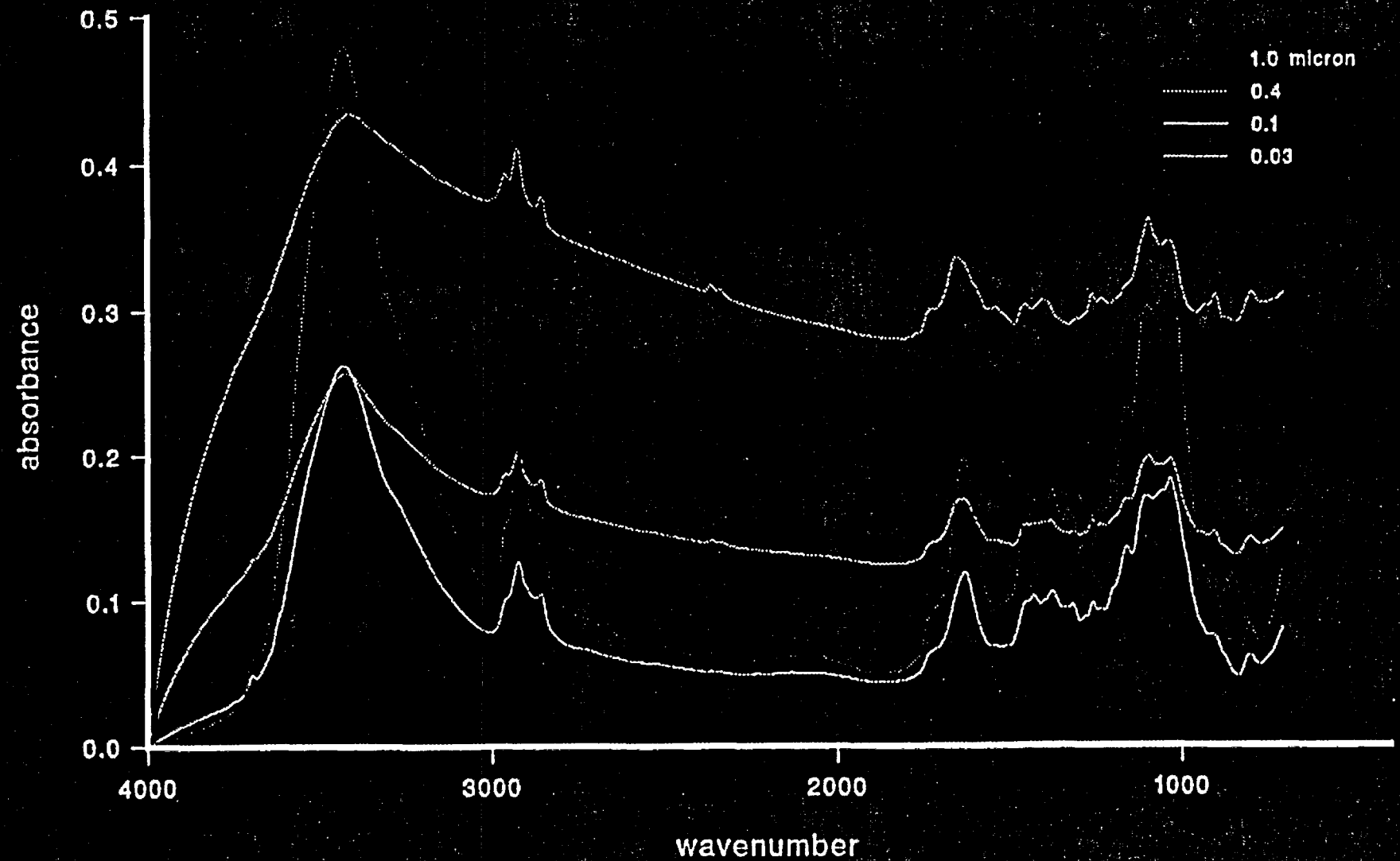
Size	MIN.	MAX	MEAN	STD. DEV.	NO.
>1	0.03	3.89	0.48	0.865	22
1-0.4	0.05	5.87	0.47	1.21	22
0.4-0.1	0.03	4.17	0.37	0.877	21
0.1-.03	0.13	1.83	0.33	0.36	21

mg/l retentate on filters with size given in micrometers

Size-Exclusion Peaks

Ash Spring	15 nm
Beatty Well	19
Cold Creek	17
Crystal Pool	>20
Fairbanks Spring	>20

Indian Springs Well



SURFACE PHYSICS AND CHEMISTRY

Gel model might be better than double layer model

reduced effective potential, ψ_o

similarly for surface complexation

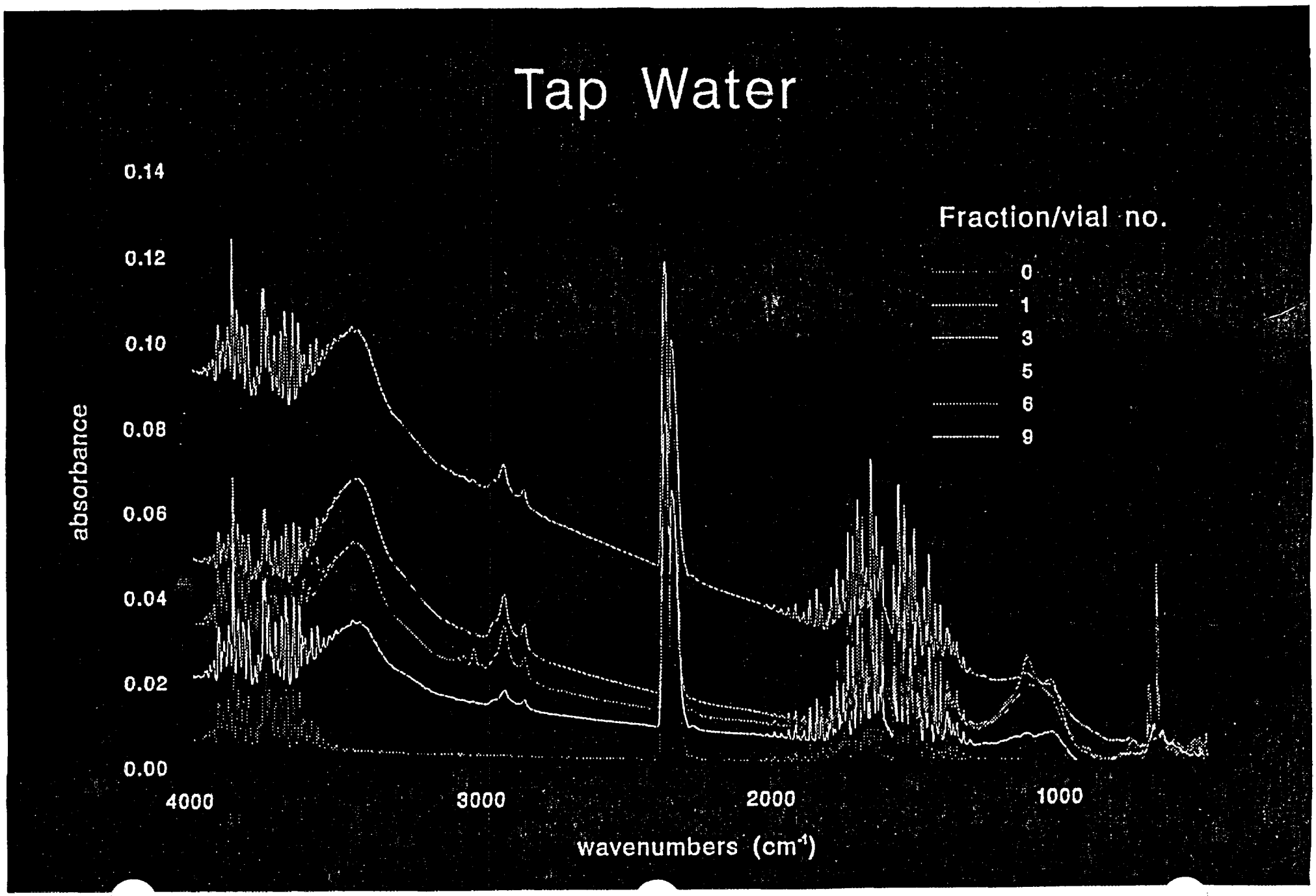
PARTICULATE ORGANIC CARBON

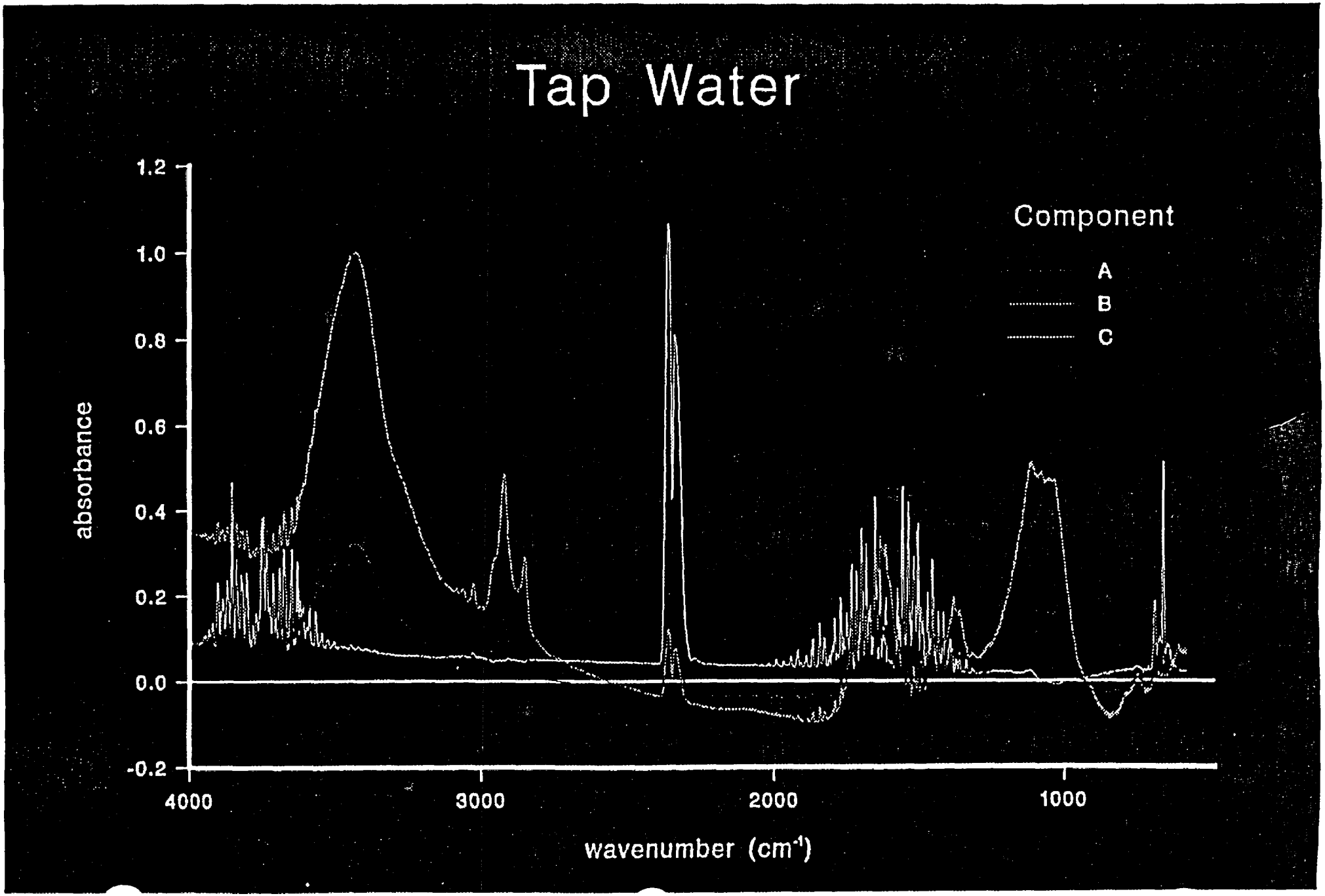
LOCATN	TOC	DOC
WELL C	0.1 (0.5)	0.1 (0.2)
UE16D	0.1 (0.5)	0.1 (0.1)
WELL 8	< 0.1 (<0.1)	<0.1 (<0.1)

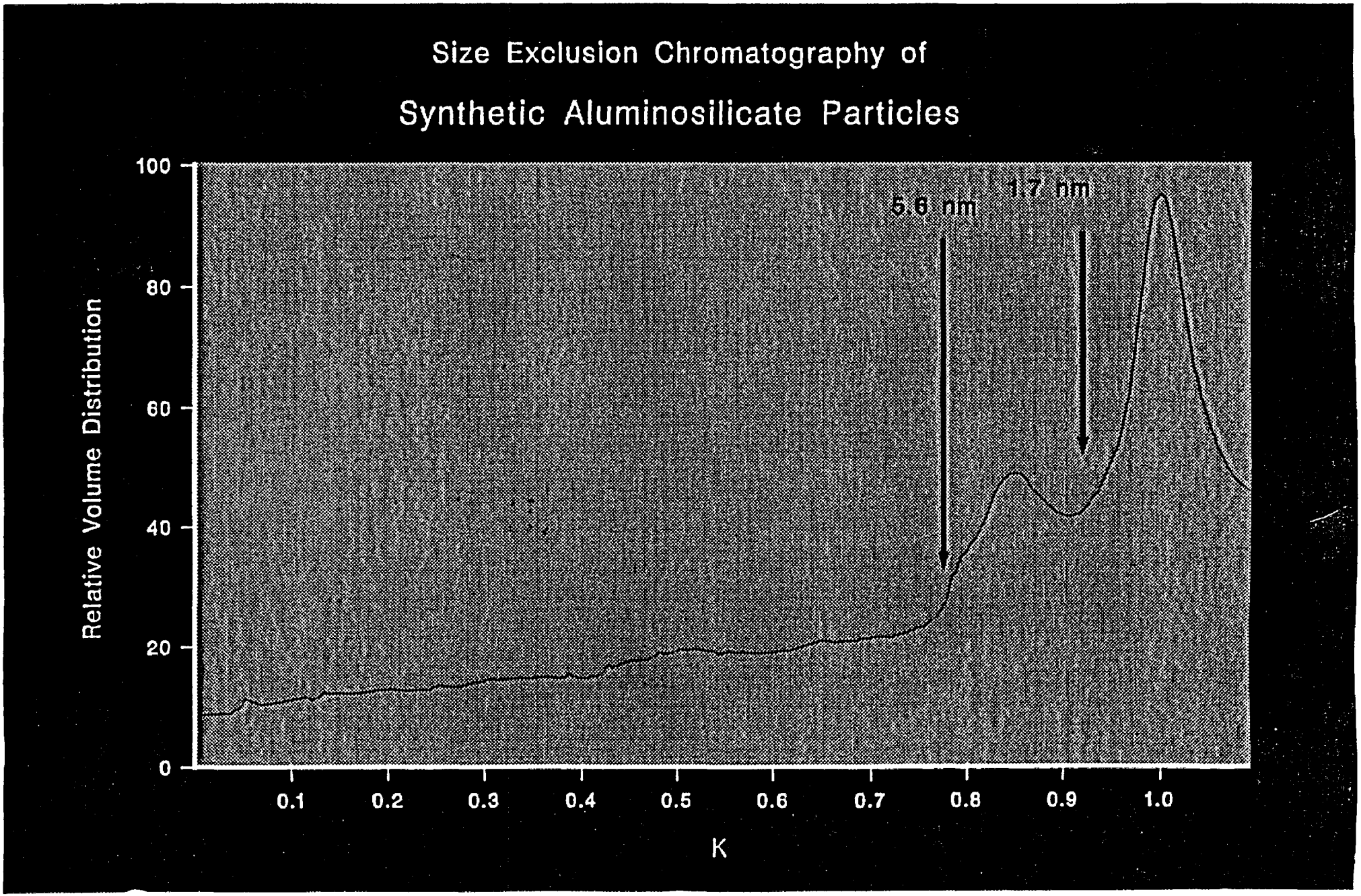
mg/l as carbon, () untreated samples

SIGNIFICANCE OF ORGANIC COATING

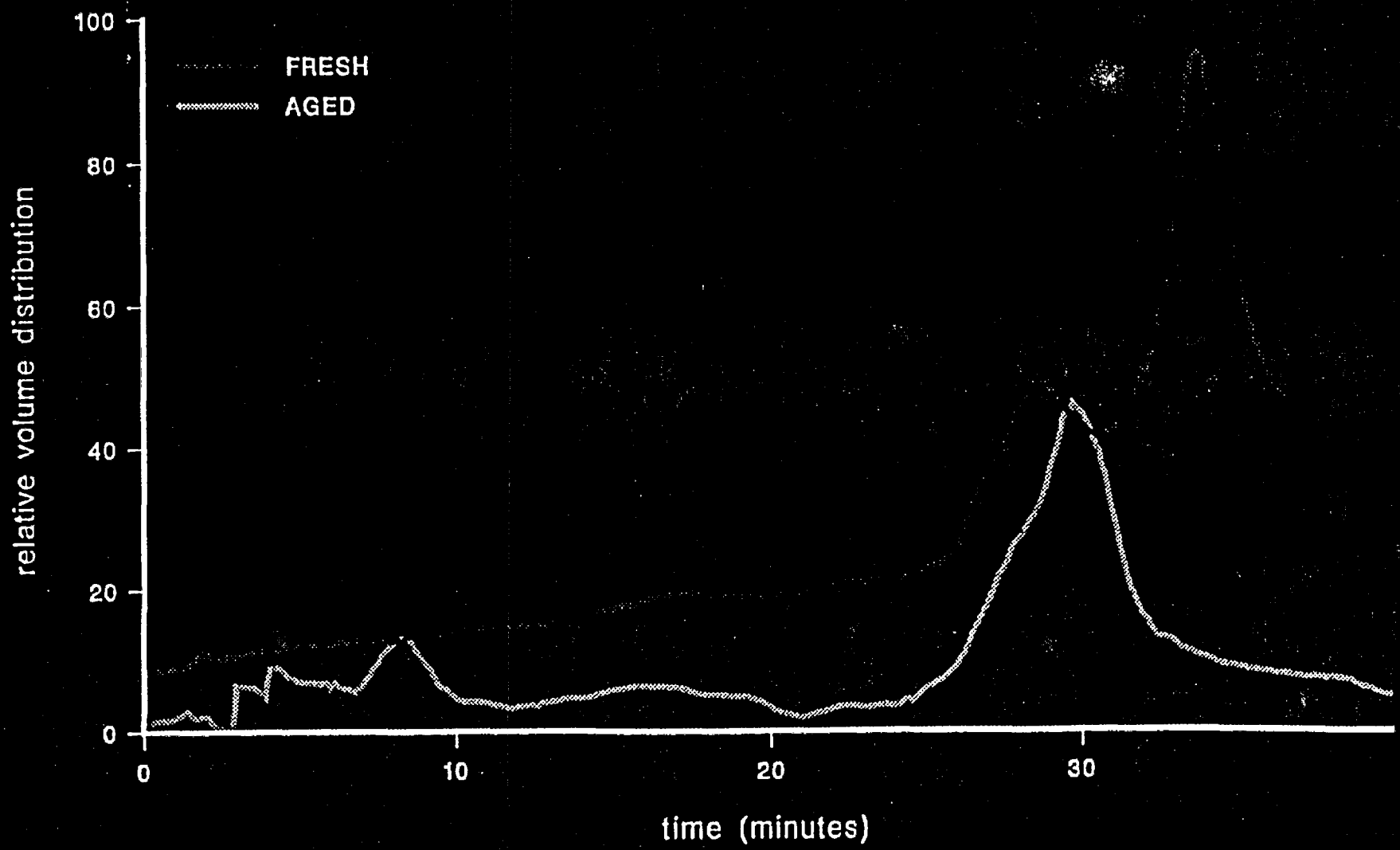
- effect stability of colloid to coagulation
- effect colloid mobility
- effect binding of contaminants to particle


Tap Water
Fraction/vial no.
0
1
3
5
6
9
absorbance
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
4000
3000
2000
1000
wavenumbers (cm-1)


Tap Water
Component
A
B
C
absorbance
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
4000
3000
2000
1000
wavenumber (cm-1)


Size Exclusion Chromatography of
Synthetic Aluminosilicate Particles
Relative Volume Distribution
100
80
60
40
20
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
K
5.6 nm
1.7 nm

Synthetic Aluminosilicate Particles



SUMMARY

colloidal particles present on avg 0.5 mg/l

composition like silica gel, some clay-like

possible organic coating

Characterization of inorganic colloids from some NTS well waters

B.E. Viani
S.I. Martin
Lawrence Livermore National Laboratory

M. ten Brink
USGS

Characterization

- Samples collected from pumped wells
- Mass determined by filtration
- Phases identified by SAED and XRD
- Individual phase compositions measured by EDXS

NTS groundwater colloids

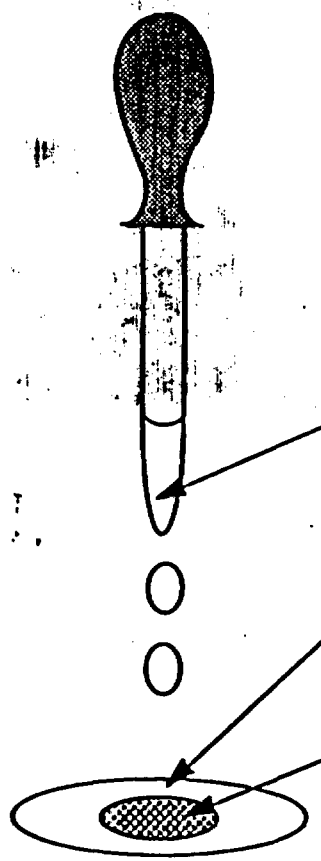
- ~1 mg/L
- Inorganic
- Fe & Si oxides, layer silicates, exotics, some that go poof
- Mineralogy related to sampling well

Colloid concentrations in some NTS waters

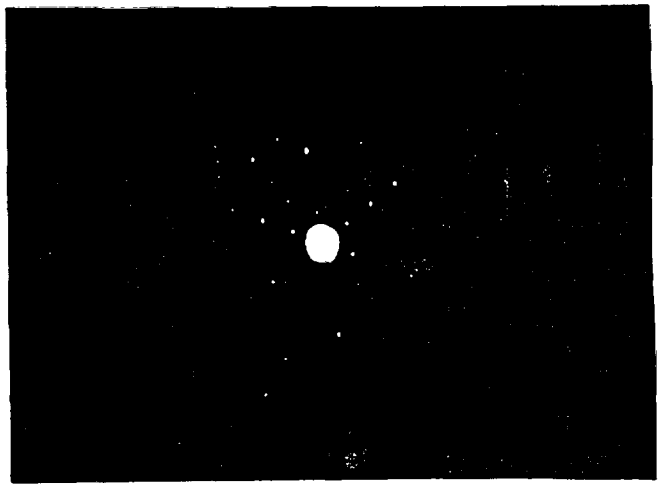
Particles captured by 0.015 µm membrane filters

Well	Particles mg/L	TDS mg/L
J-13	1.4	281
UE-19c.	3.1	151
UE-20n-1	5.1	255
5c	1.1	381

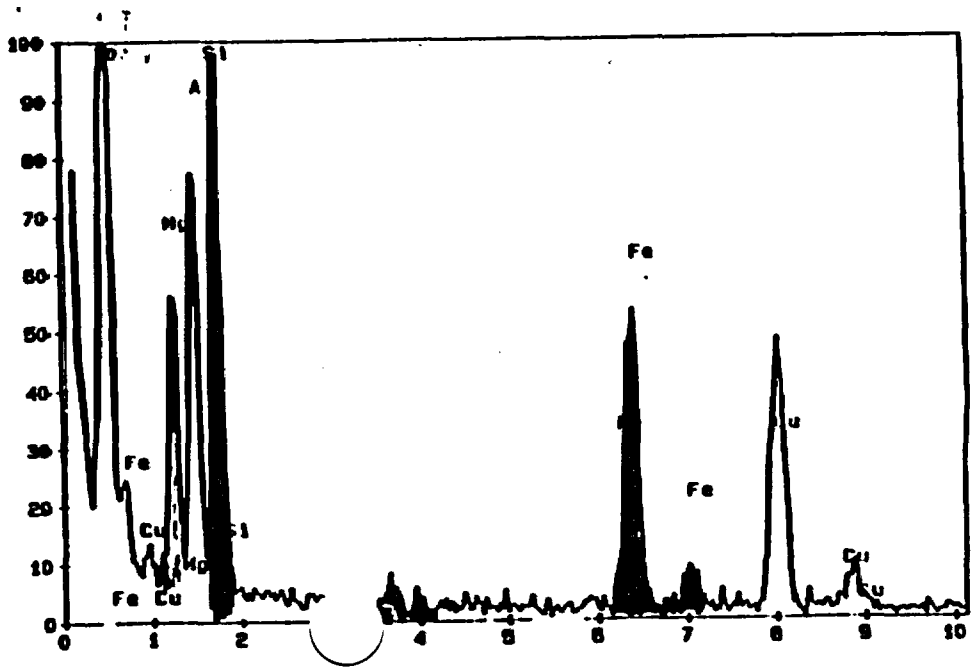
Preparation of samples for TEM analysis



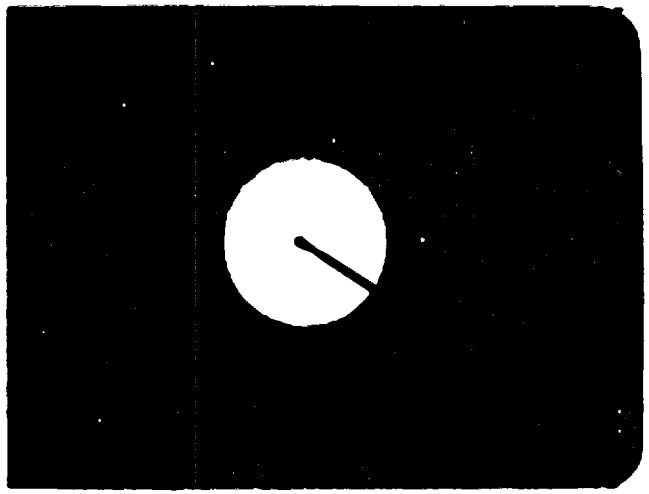
Well J-13 - Mica



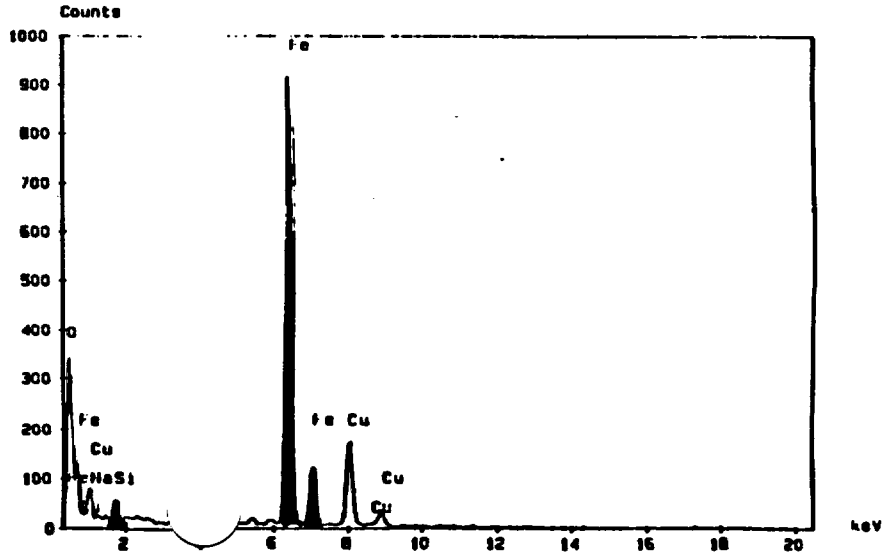
1.0 µm



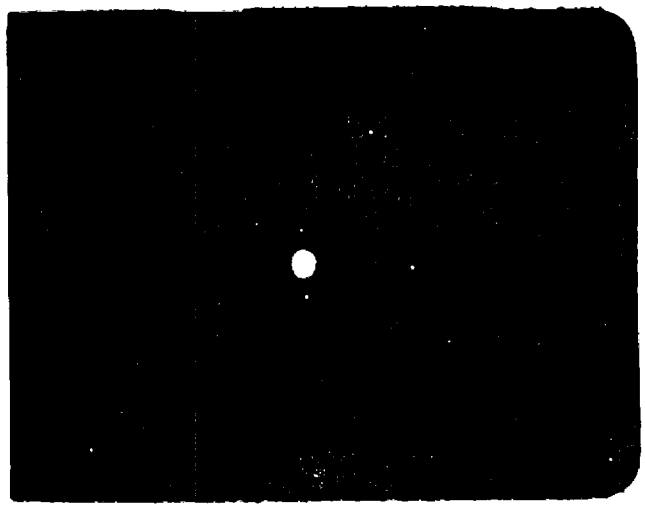
Well J-13 - Hematite

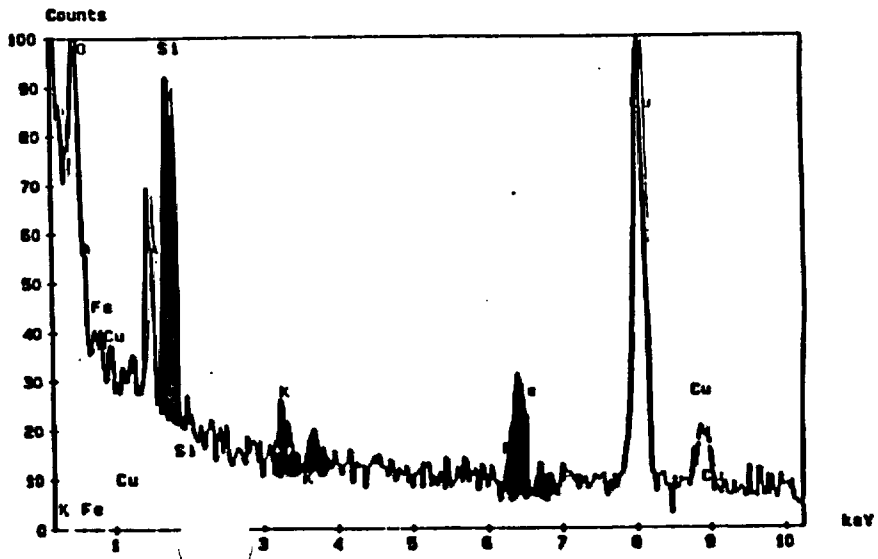


1.0 µm

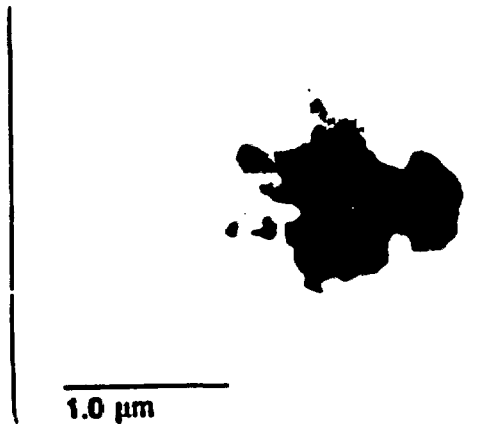


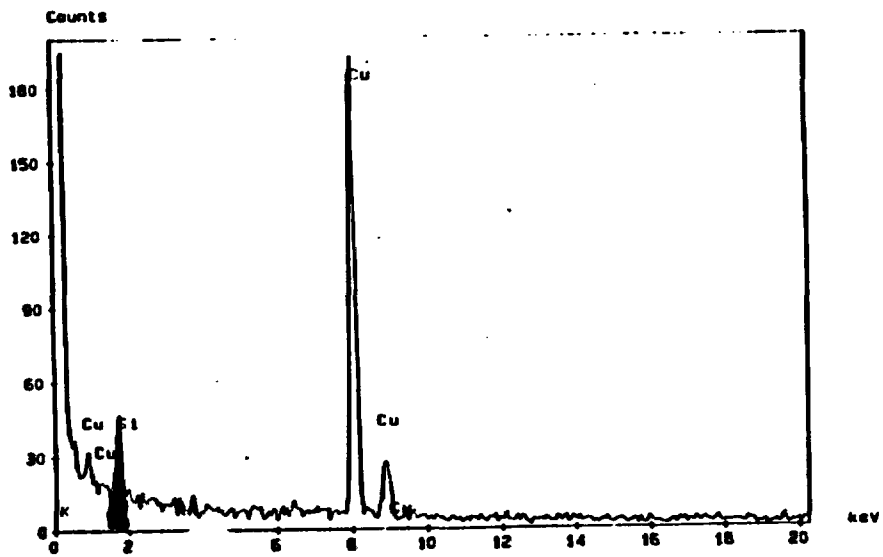
Well J-13 - Illite



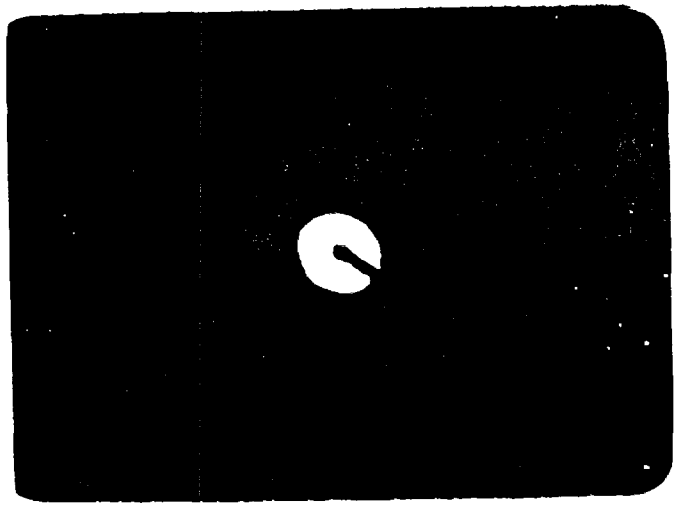


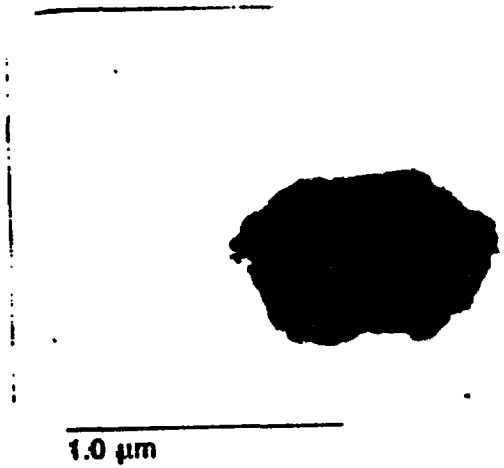
Well 19c - Cristobalite

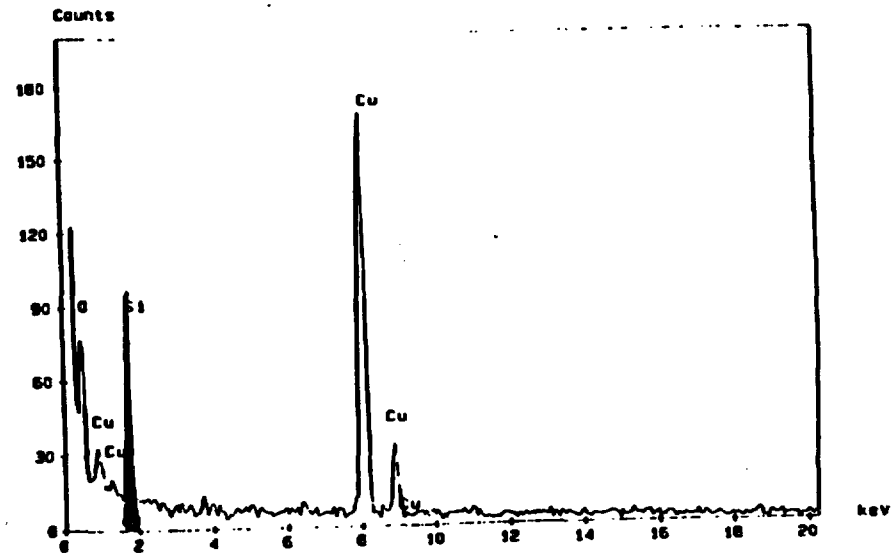




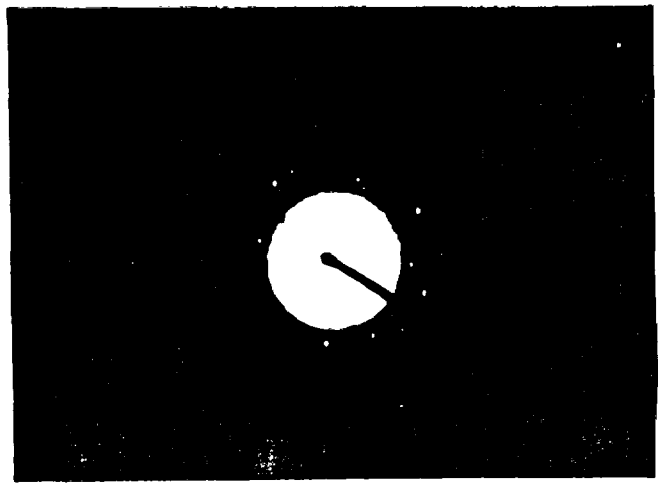
Well 19c - Amorphous silica



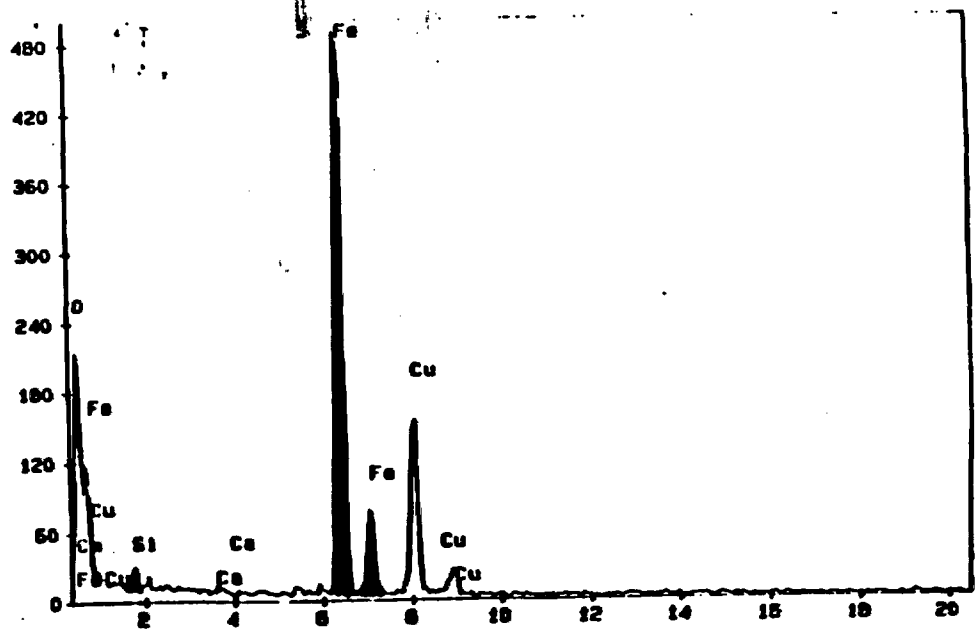




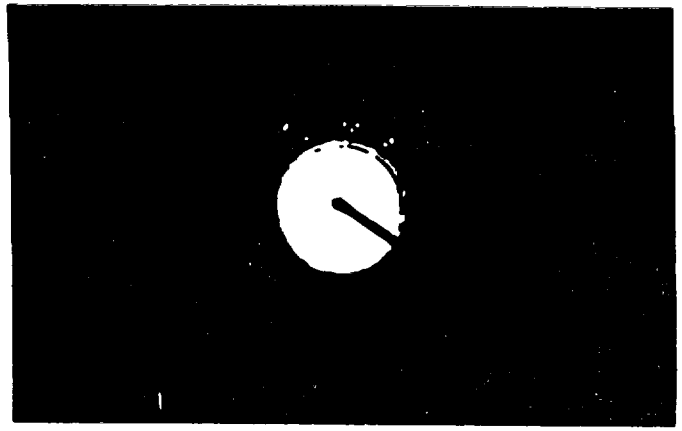
Well 5c - Hematite



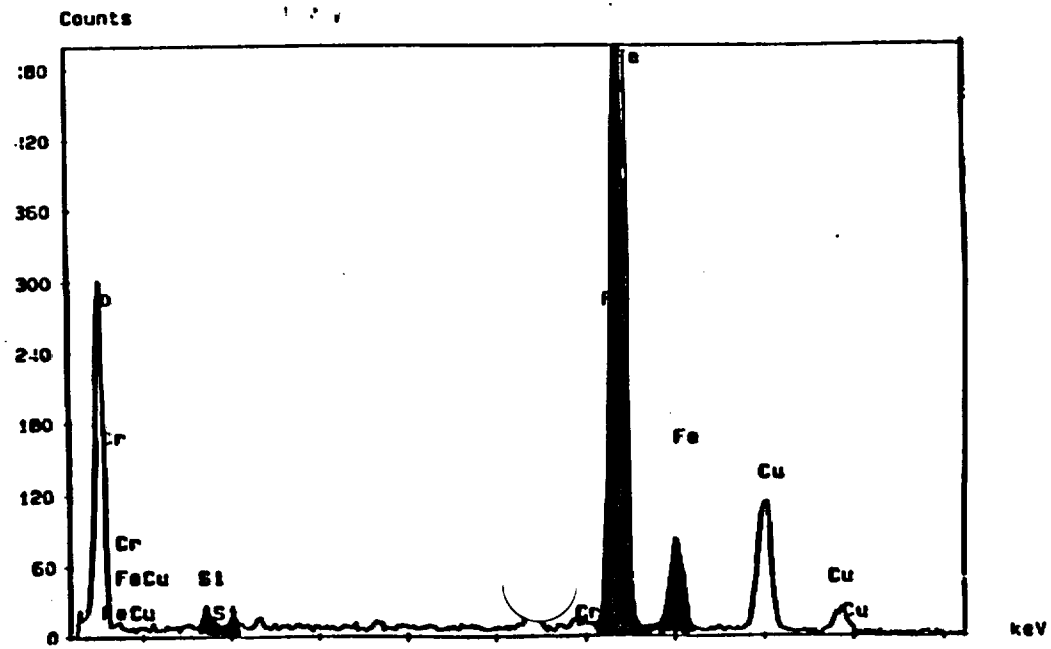
0.5 µm



Topopah Springs tuff fracture flow experiment - 0.05 m/day - Hematite

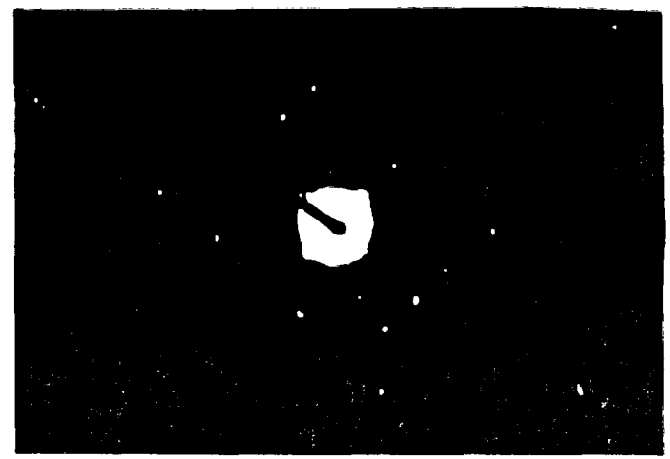


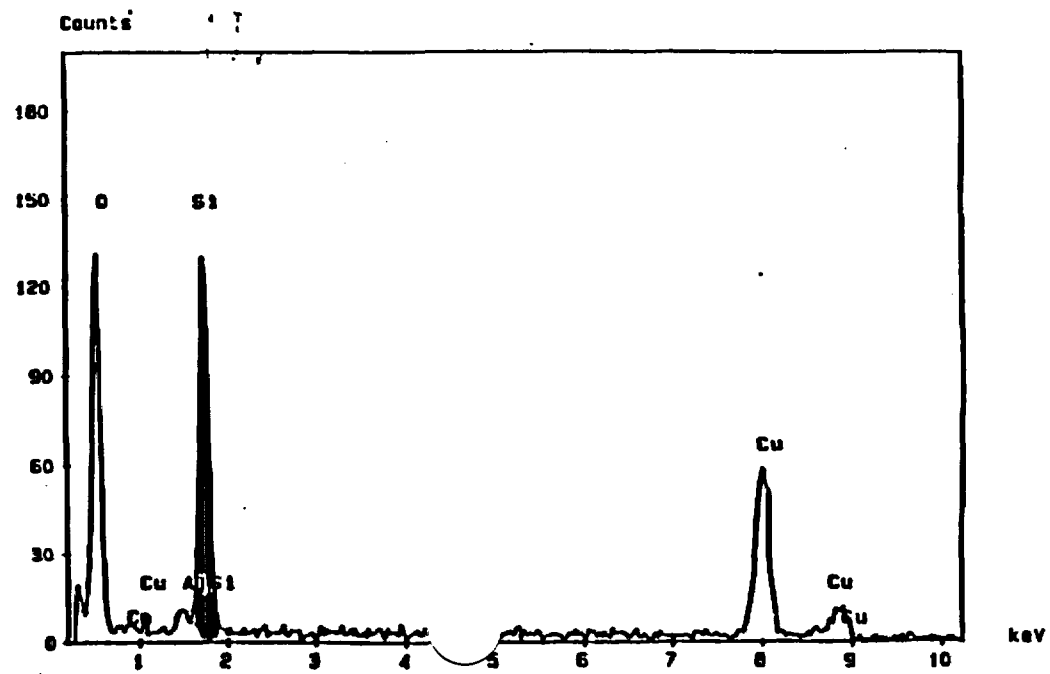
1.0 µm



Topopah Springs tuff fracture flow experiment - 0.05 m/day - Quartz

1.0 µm





Conclusions

- Most of the inorganic phases identified are consistent with minerals in formation.
- Contamination inferred from presence of exotic phases or compositions.
- Different wells display differences in mineralogy.
  - Well J-13: Iron oxides, layer silicates, and Ca-phase
  - Well 5c: Iron oxides and layer silicates
  - Well 19c: Silicon oxides
- Particles that are damaged by the electron beam, and those that are not captured by the holey-carbon-film are not sampled.
- Inorganic colloids in "clean" groundwaters and those generated in core-flow experiments are readily detected and identified using this method.

Direct Quantification of Organic Material in NTS Well Waters

Cynthia E. A. Palmer
Robert J. Silva
Howard L. Hall
Gregory L. Klunder
Richard E. Russo
David A. Wruck

Total organic carbon in NTS well water

	Sample Preservation Method				
NTS Well	A	B	C	D	E
4	0.229	0.113	0.00951	–0.0626	0.0203
8	0.247	0.507	–0.0587	——	–0.0154
16D	0.227	0.135	0.00914	–0.0386	0.0157
20W	0.254	0.153	–0.0213	–0.0776	0.0262
Cane Springs	0.551	0.416	0.254	0.233	0.268

Methods
- A: H_3PO_4, light, ambient temperature, plastic bottle
- B: H_2SO_4, dark, cold room, plastic bottle
- C: H_2SO_4, dark, cold room, glass bottle (EPA protocol)
- D: H_2SO_4, light, ambient temperature, glass bottle
- E: $NaNO_3$, H_2SO_4, dark, cold room, glass bottle (Whitbeck protocol)

Note: Aldrich Humic Acid (Na salt) 41.78% C by weight

Technical Issues

- Appropriate "zero"

- High concentration of inorganic carbon measured before low organic carbon concentration
  - adjust pH to ~ 3
  - bubble Ar through sample ~ 30 minutes
  - three determinations of [TOC]

- Standard Additions

Analyses of H_2O Background

	Detector Response (mV)
Milli-Q H_2O B. 281	32.391
Milli-Q H_2O B. 222	52.054
Milli-Q H_2O B. 151	51.398
HPLC H_2O	20.484
lowest NTS groundwater	13.389

Charge Transfer Fluorescence Determination

Groundwater
< 0.20 ppm TOC
+
100 ppm Eu^{+3}

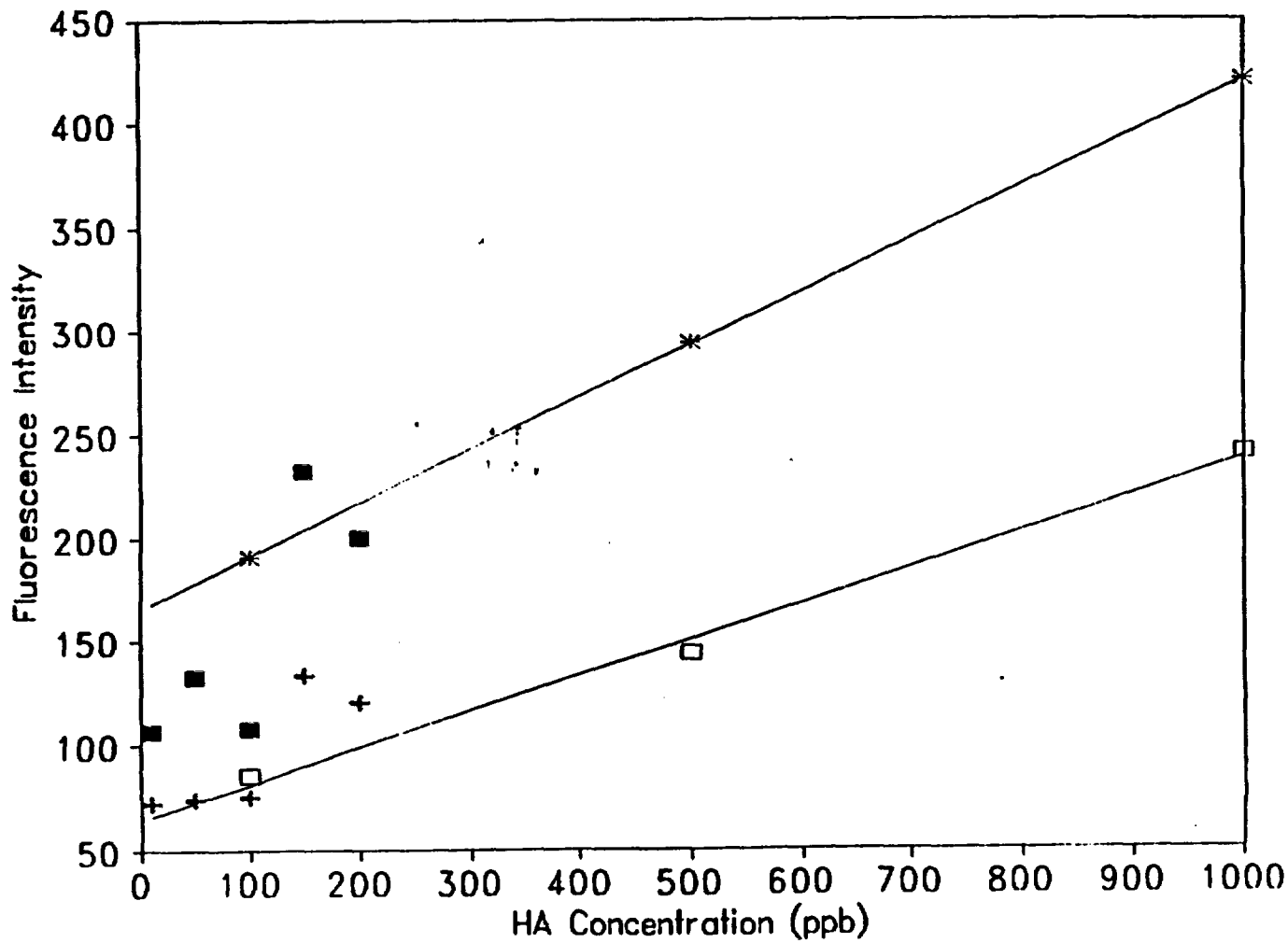
$\xrightarrow[\text{Formation}]{\text{Complex}}$ Eu-organic

$\xrightarrow[\text{of organic ligand with 354 nm light}]{\text{Laser Excitation}}$ Eu-organic*

Eu-organic* $\xrightarrow[\text{Transfer}]{\text{Charge}}$ Eu-organic* $\xrightarrow{\text{Fluorescence}}$ Eu-organic

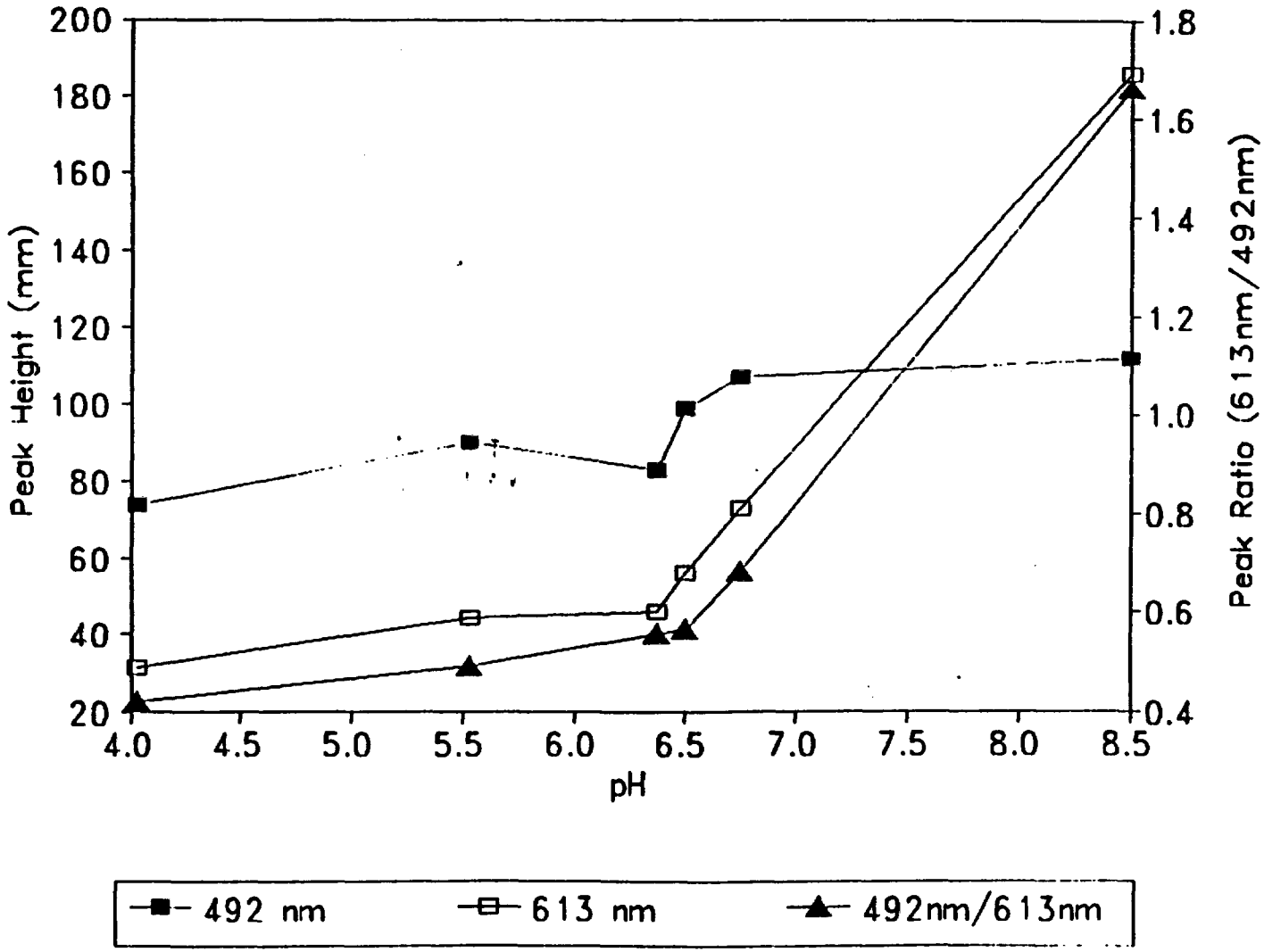
Effects of varying concentration of Humic Acid

$[Eu^{+3}] = 100$ ppm pH = 5.24



Effect of varying pH

$[Eu^{+3}]$ = 100 ppm [HA] = 300 ppb

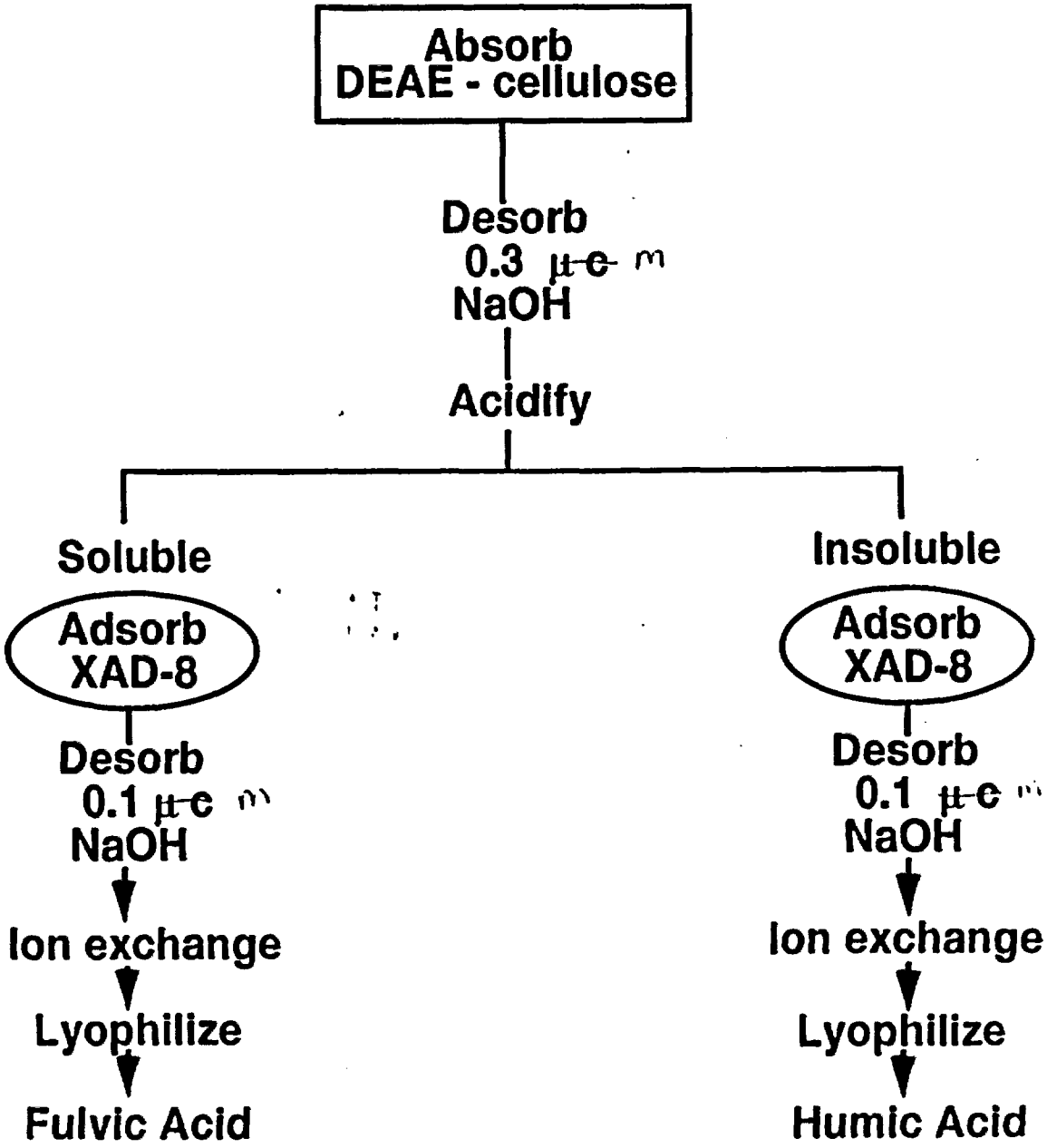


Technical Issues

- Precipitation formed in well water samples
- Photodegradation of material in well water samples
- * Eu fluorescence observed

- Tunable excitation
- Less powerful excitation source

Swedish Effort



Technical Issues

- No acidification of well water required
- Unsuccessful at rinsing DEAE free of organic material before loading well water

---

- Laser light scattering
- Flow cytometry

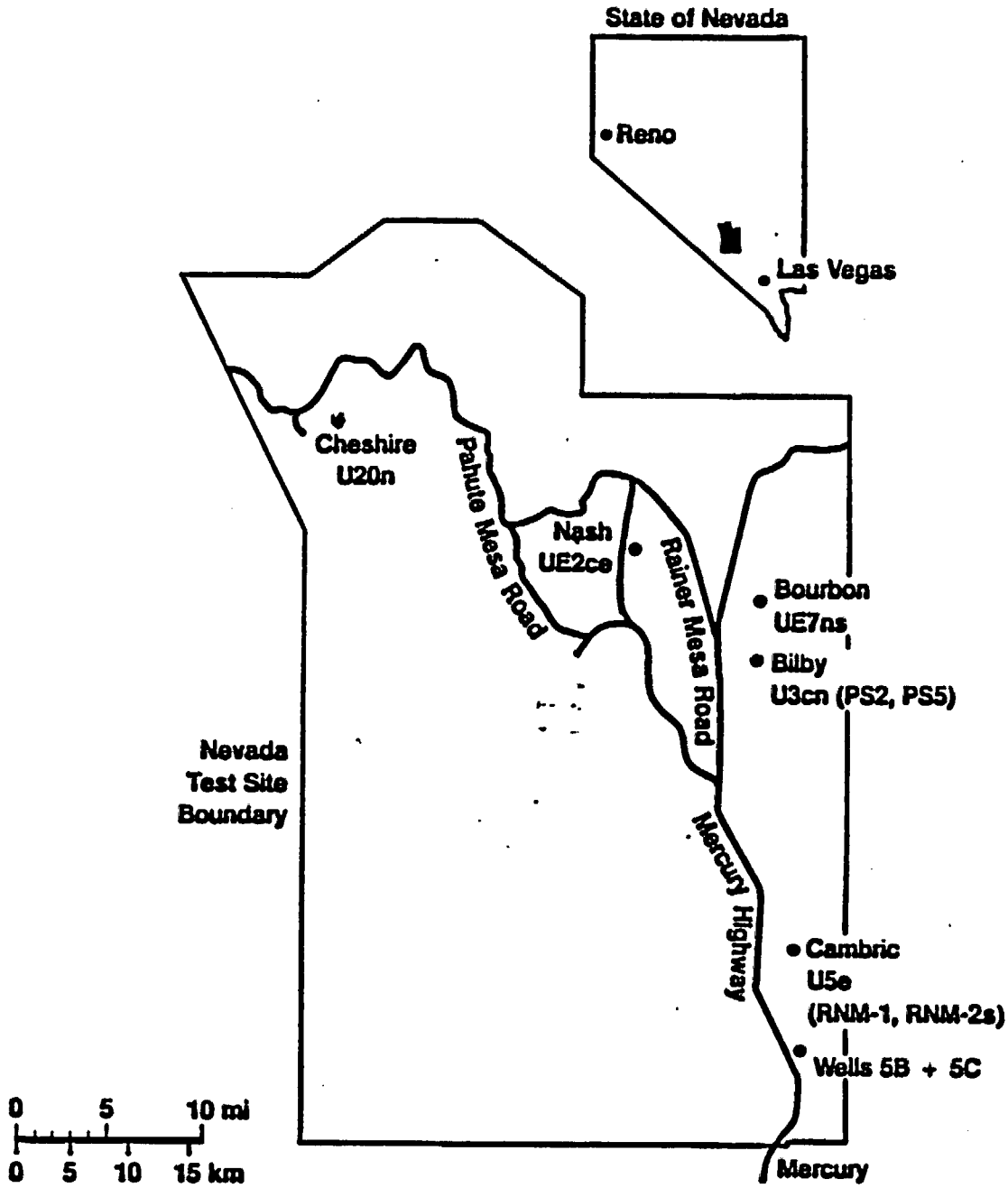
RADIONUCLIDE MIGRATION AT THE NEVADA TEST SITE

JAMES R. HUNT

DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF CALIFORNIA AT BERKELEY

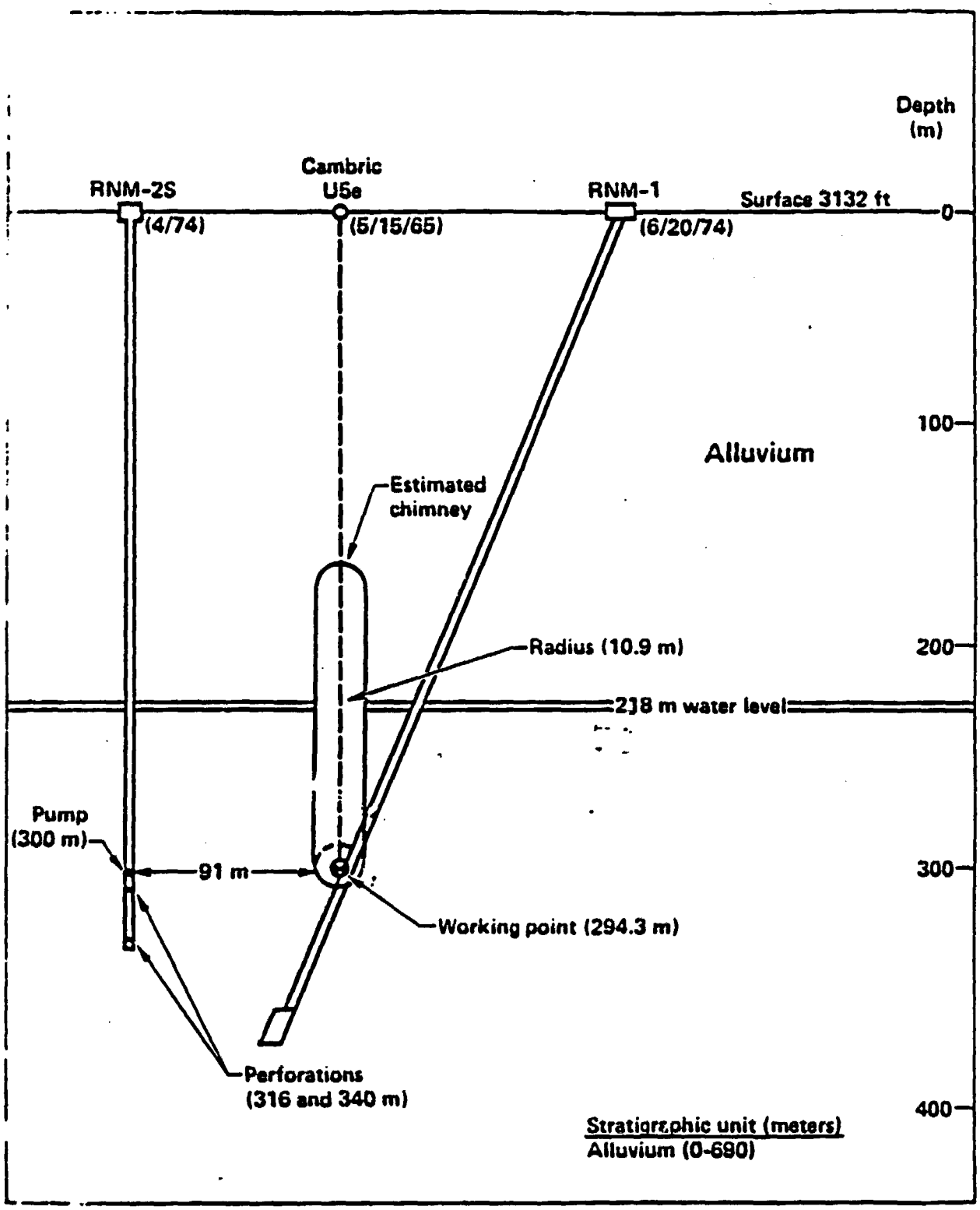
SUPPORT:
HYDROLOGY AND RADIONUCLIDE MIGRATION PROGRAM
LAWRENCE LIVERMORE NATIONAL LABORATORY

NEVADA TEST SITE

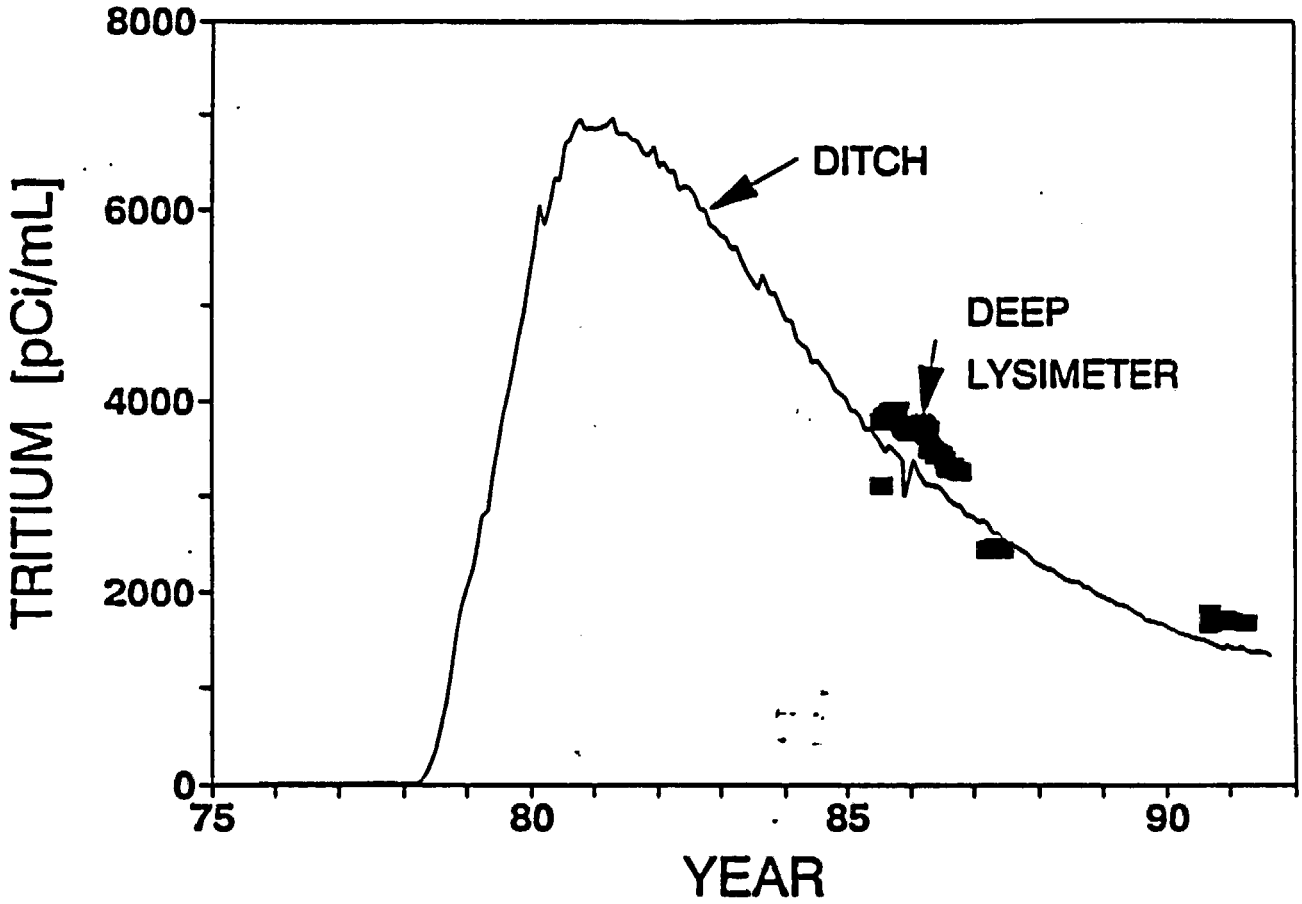


LLNL

CAMBRIC SITE CROSS SECTION



CAMBRIC


8000
6000
4000
2000
0
TRITIUM [pCi/mL]
DITCH
DEEP
LYSIMETER
75
80
85
90
YEAR

Hydrology and Radionuclide Migration Program 1989 Progress Report, Compiled by K.V. Marsh, Aug. 1992. UCRL-53779-89, LLNL

CHESHIRE.

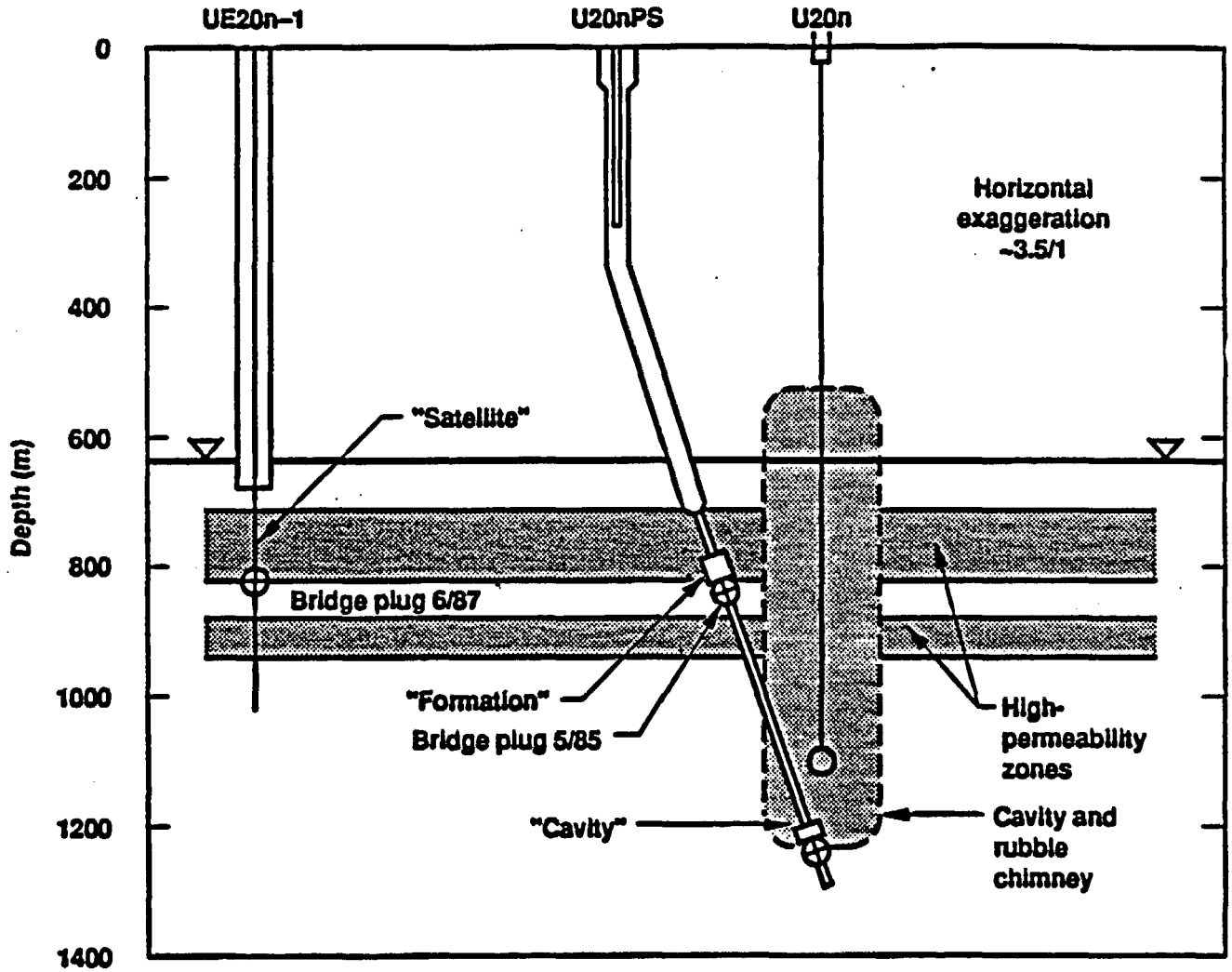


Figure 2.1. Vertical section of the Cheshire study area, showing schematically the relationship between the UE20n-1 satellite well and the cavity and formation sampling points in the U20nPS hole. The hypothesized direction of groundwater movement is upward from the cavity through the chimney to the upper permeable zone, and then laterally to the formation and satellite sampling points.

PARTICLE CONCENTRATIONS BY SEQUENTIAL ULTRAFILTRATION

LOCATION	SIZE RANGE	CONCENTRATION
CAVITY	200-6 nm	55 mg/L
	50-3	10
FORMATION	50-3	4

Buddemeier and Hunt (1988)

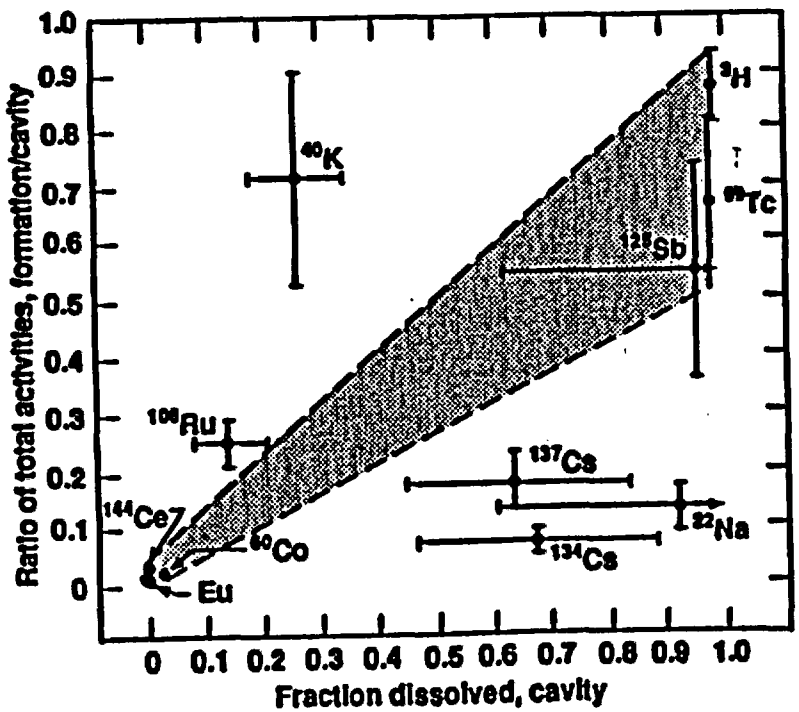
TRANSPORT OF RADIONUCLIDES FROM THE CAVITY

RADIONUCLIDE	HALF LIFE [y]	FORMATION TO CAVITY RATIO	FRACTION DISSOLVED IN CAVITY	SATELLITE TO CAVITY RATIO
^{3}H	12.26	0.86	1.0	1.15
^{22}Na	2.6	0.126	0.93	
^{60}Co	5.27	0.034	0.021	
^{106}Ru	1.02	0.25	0.14	
^{125}Sb	2.76	0.54	0.97	0.22
^{134}Cs	2.065	0.072	0.68	
^{137}Cs	30.17	0.17	0.65	0.001
$^{152,154,155}Eu$	4.7-13.4	0.025	<0.01	

Buddemeier and Hunt (1988)

Hydrology and Radionuclide Migration Program 1988 Progress Report, Compiled by K. V. Marsh., march 1992 UCRL-53779-88 LLNL.

CHESHIRE RADIONUCLIDES

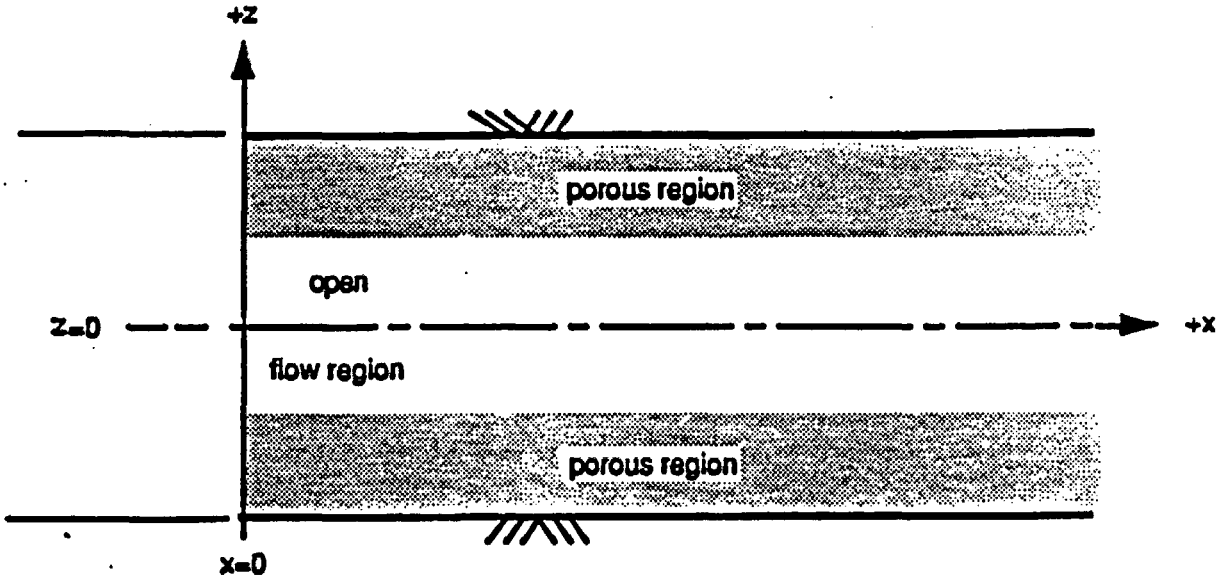


Buddemeier and Hunt (1988)

Problems of Cheshire Data Set

1. Pumped samples.
2. Stored samples
3. Ultrafiltration is energetic
4. migration or prompt injection of gas
5. Well Casings

PARTIALLY CLOGGED FRACTURE



Kessler and Hunt (submitted)

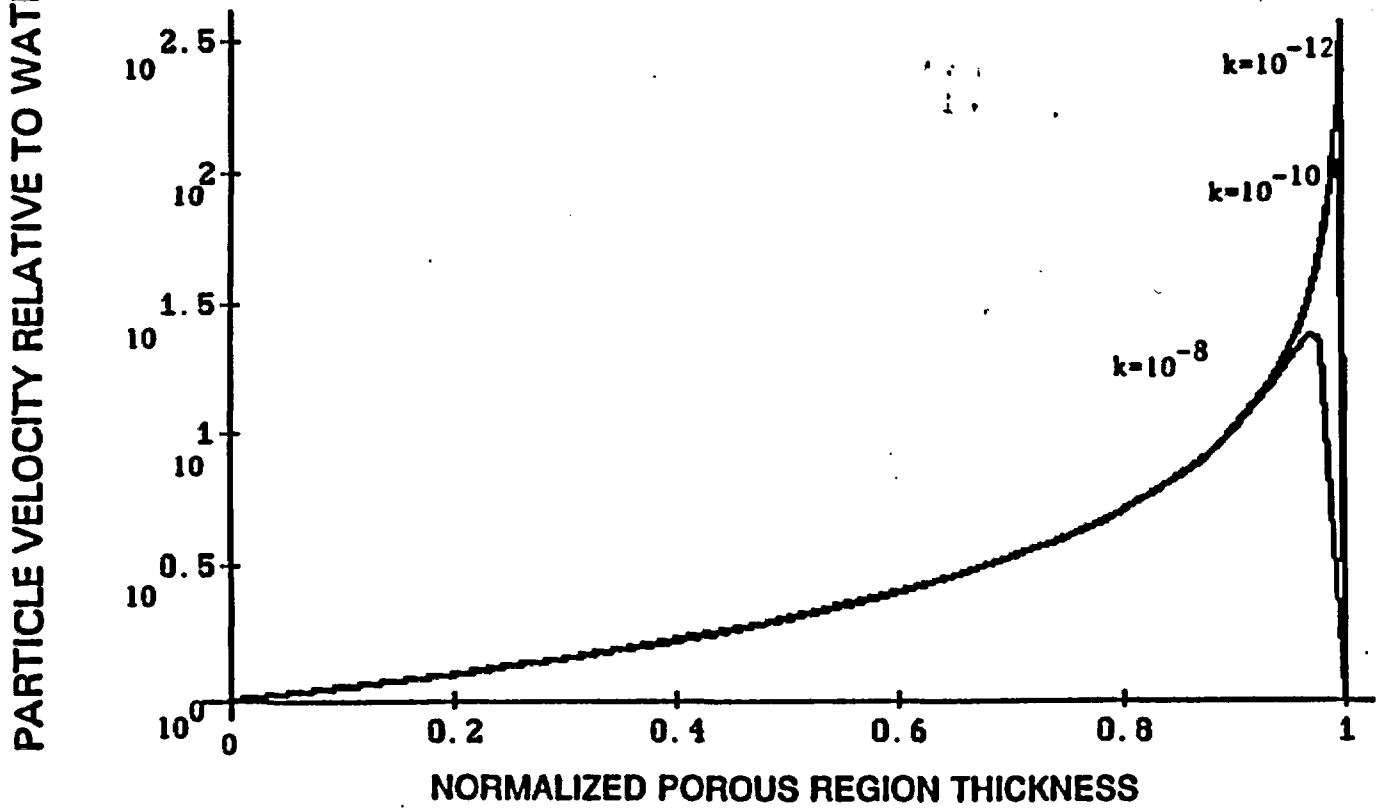
PARTICLES MOVE FASTER THAN WATER IF EXCLUDED FROM POROUS REGION

APERTURE = 0.1 cm

POROSITY = 0.95

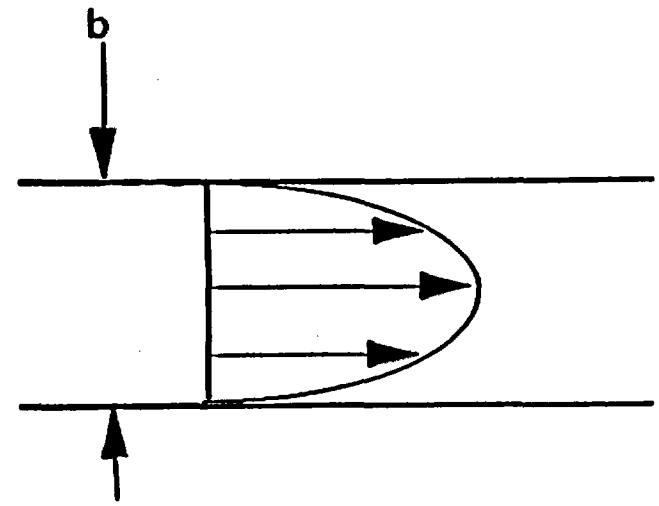
CONSTANT PRESSURE GRADIENT

PERMEABILITY, k (cm^2)



Keesler and Hunt (submitted)

TAYLOR DISPERSION IN FRACTURE



OVERALL LONGITUDINAL DISPERSION

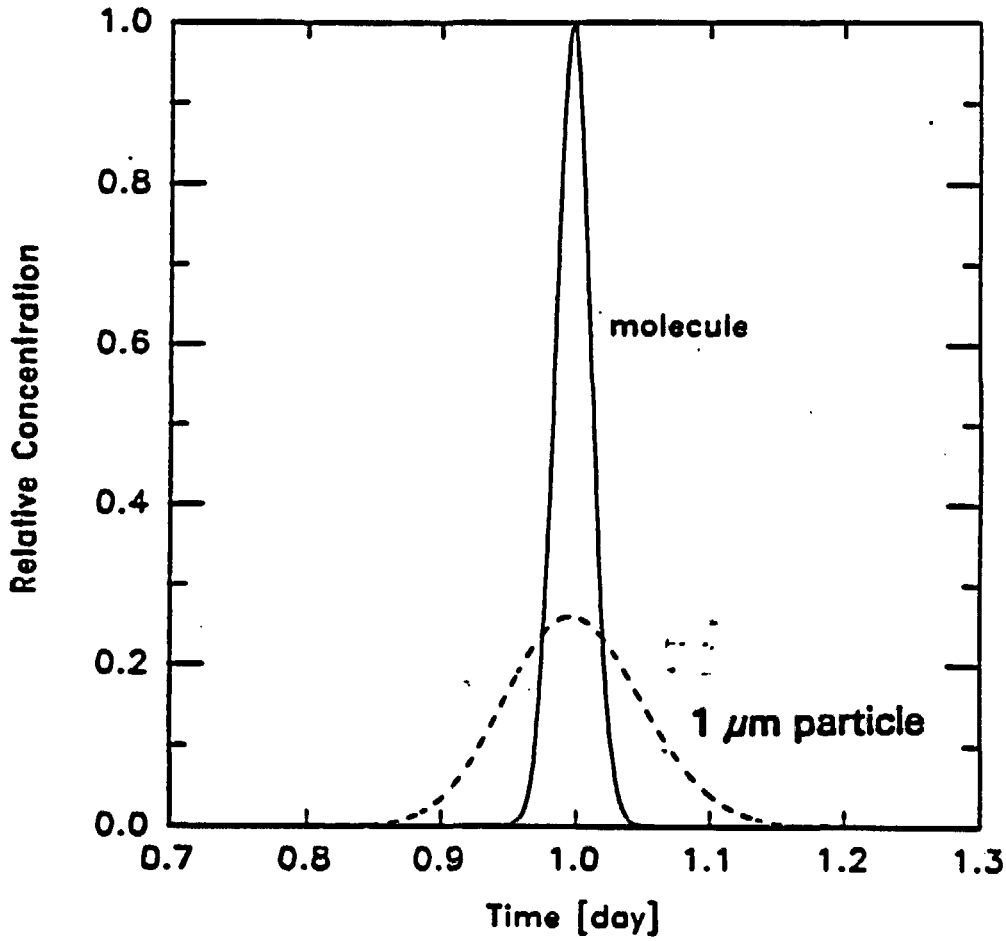
$$D_L = D_b + \frac{U^2 b^2}{210\, D_b}$$

D_b = BROWNIAN OR MOLECULAR DIFFUSIVITY

= 10^{-5} cm^2/s FOR SOLUTE

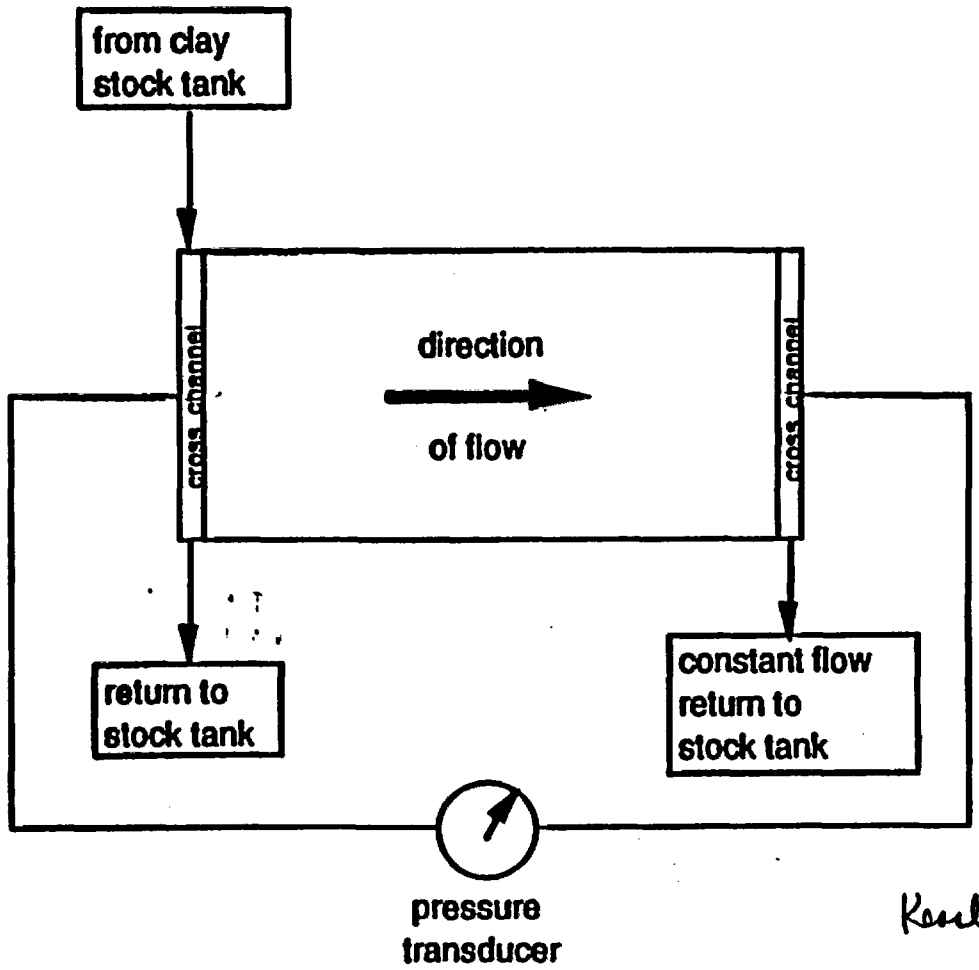
= 4×10^{-9} cm^2/s FOR 1 μm PARTICLE

BREAKTHROUGH CURVES FOR U = 1 m/d
AND 1 m DOWNSTREAM



Kessler and Hunt (submitted)

SCHEMATIC OF PARALLEL PLATE FLOW SYSTEM



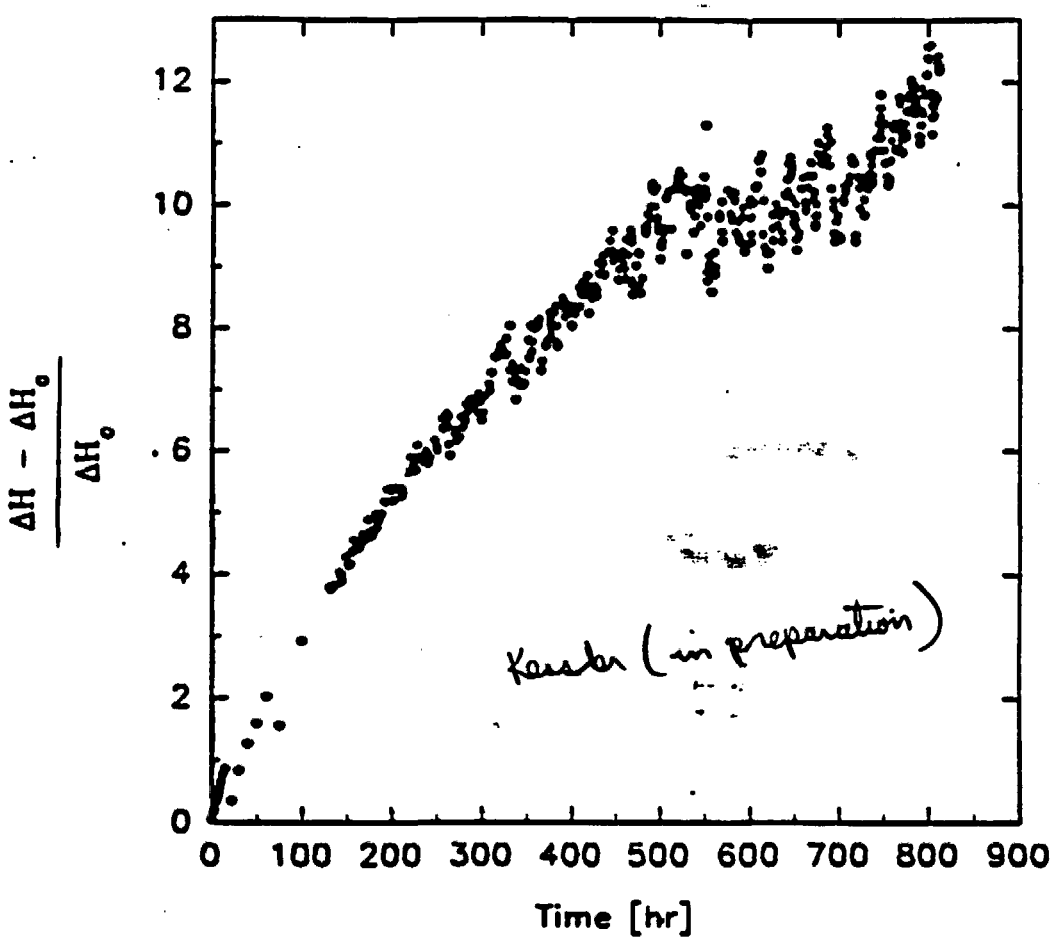
Kessler (in preparation)

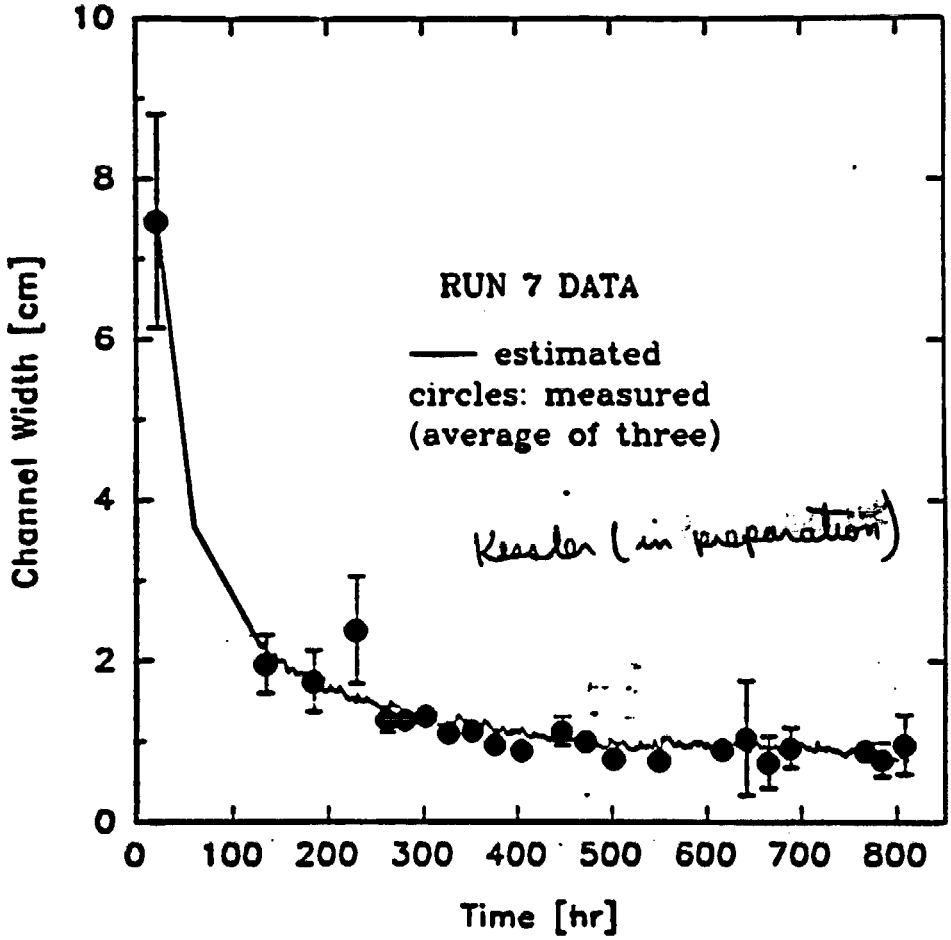
PARALLEL PLATES - Top View

EXPERIMENTAL PARAMETERS

- Parallel plate dimensions:
  - aperture, b = 0.026 cm
  - width, W_{TOT} = 10.2 cm
  - length, L = 25.4 cm
- Approach velocity of 184 m/day (flow rate = 3.38 mL/min)
- Montmorillonite, initial concentration = 500 mg/L
- 0.1M NaCl, 0.1M $CaCl_2$, 1g/L NaN_3
- Experiment duration of approximately 820 hours

RUN 7 NORMALIZED HEAD VERSUS TIME DATA




RUN 7 DATA
—— estimated
circles: measured
(average of three)
Kessler (in preparation)
Channel Width [cm]
Time [hr]
0
2
4
6
8
10
0
100
200
300
400
500
600
700
800

FOR A PARTIALLY CLOGGED FRACTURE

PARTICLE VELOCITY > SOLUTE VELOCITY

PARTICLE DISPERSION > SOLUTE DISPERSION

∴ PARTICLES ARRIVE SOONER THAN SOLUTES

EXPERIMENTALLY, WHEN SOLIDS OCCUPY 1% OF FRACTURE VOLUME, HEAD LOSS INCREASES BY A FACTOR OF 10

EXPECT COMPLETE CLOGGING IF HEAD LOSS IS CONSTANT

References.

Mc Dowell-Boyer, Hunt, Sitar (1986) Particle transport through porous media, Water Resources Research 22, 1901-1921.

Buddemeier + Hunt (1988) Transport of colloidal contaminants in groundwater: radionuclide migration at the Nevada Test Site. Applied Geochemistry. 3, 535-548.

Mc Dowell-Boyer (1992) Environmental Science and Technology, January.

Hunt, Huang, and McDowell-Boyer (1993) Solids accumulation during deep bed filtration, Environmental Science and Technology, June.

Kessler and Hunt (submitted) Dissolved and Colloidal Contaminant Transport in a partially clogged fracture, under review Water Resources Research

J.H. Kessler (in preparation) PhD Thesis, U.C. Berkeley.

G.J. Nimz and J.L. Thompson (1992) Underground Radionuclide migration at the Nevada Test Site., DOE/NV-346, UC-703.

Will colloids move 100's m under Yucca Mtn.?

IF Flow is NOT PULSED

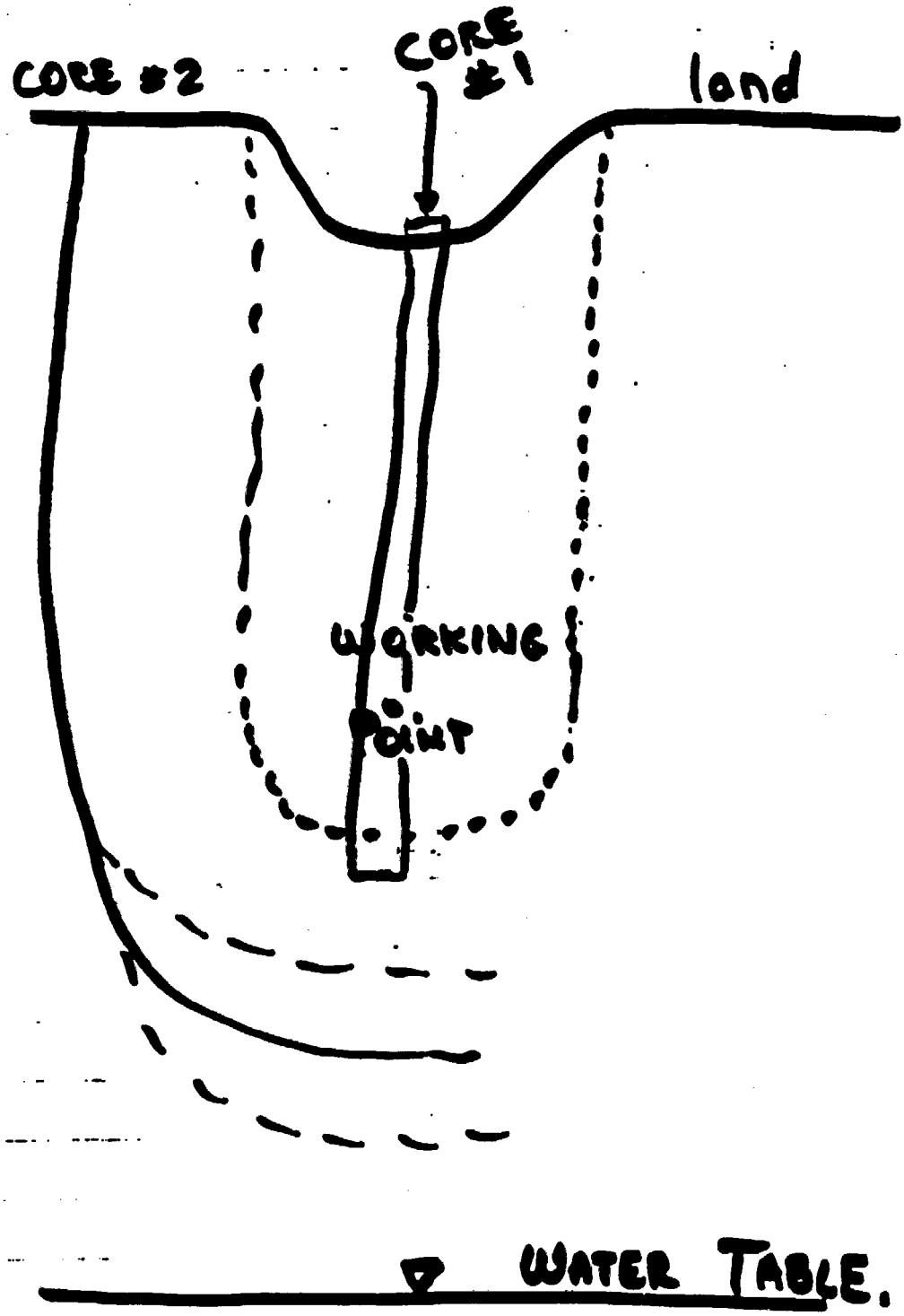
IF Aqueous Chemistry is NOT ALTERED

IF ground not shaken

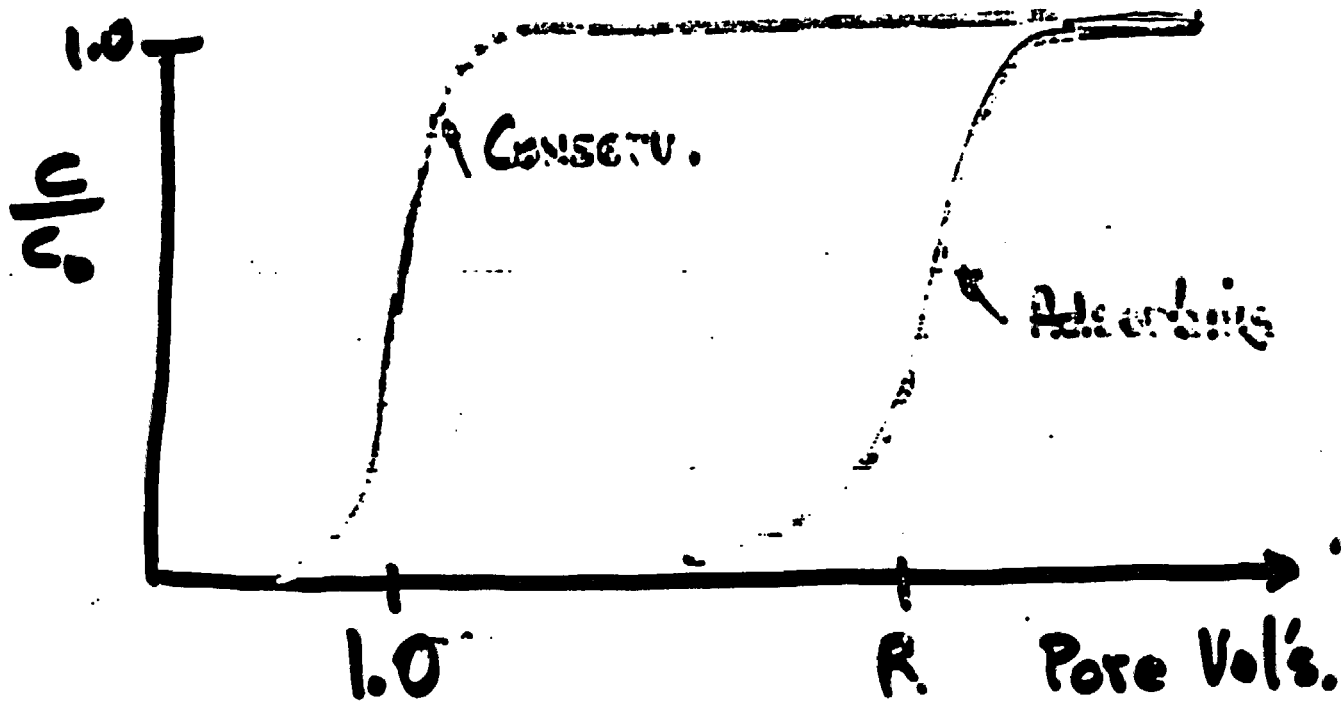
Then NO

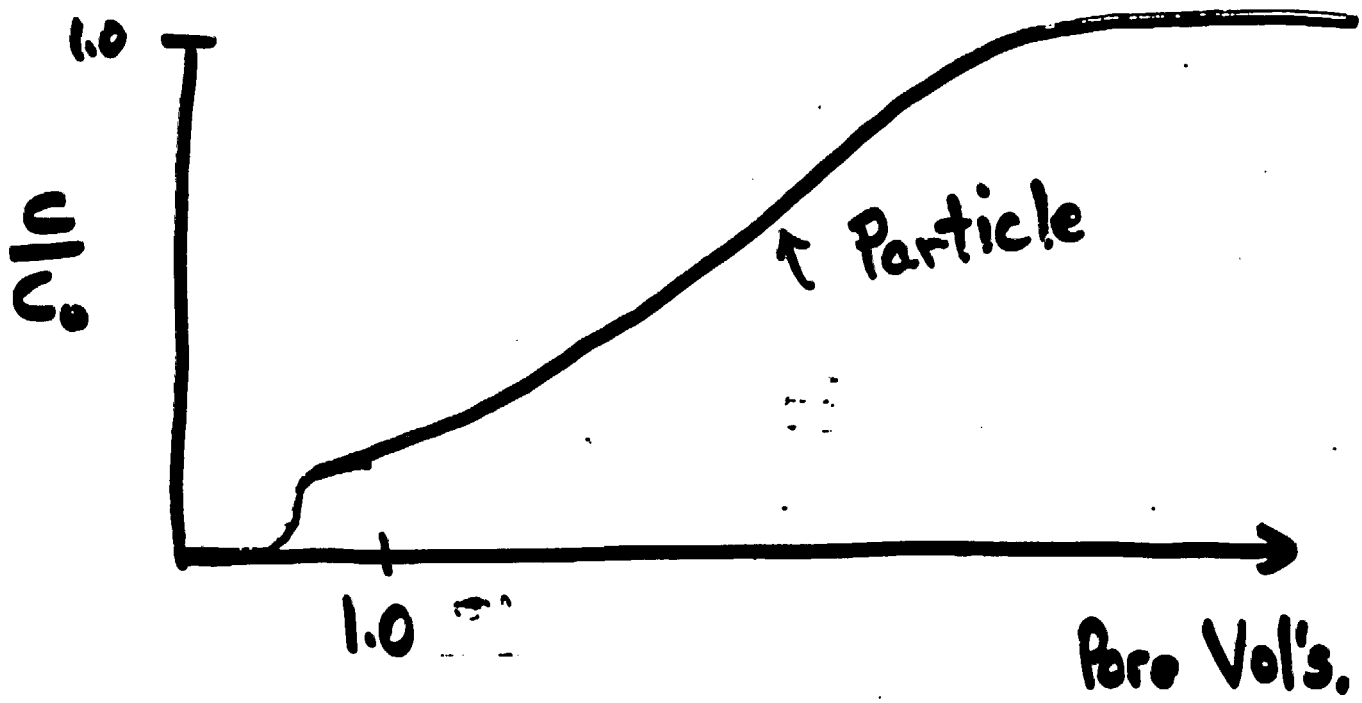
Because colloids will deposit and clog fractures.

UNSAT. ZONE TRANSPORT AT NTS



Column Breakthru's.





Characteristics and Mobility of Actinides in an Aquifer in a Semi-arid Region

by

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Environmental Science Group
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Based on Cooperative Study
with
Argonne National Laboratory

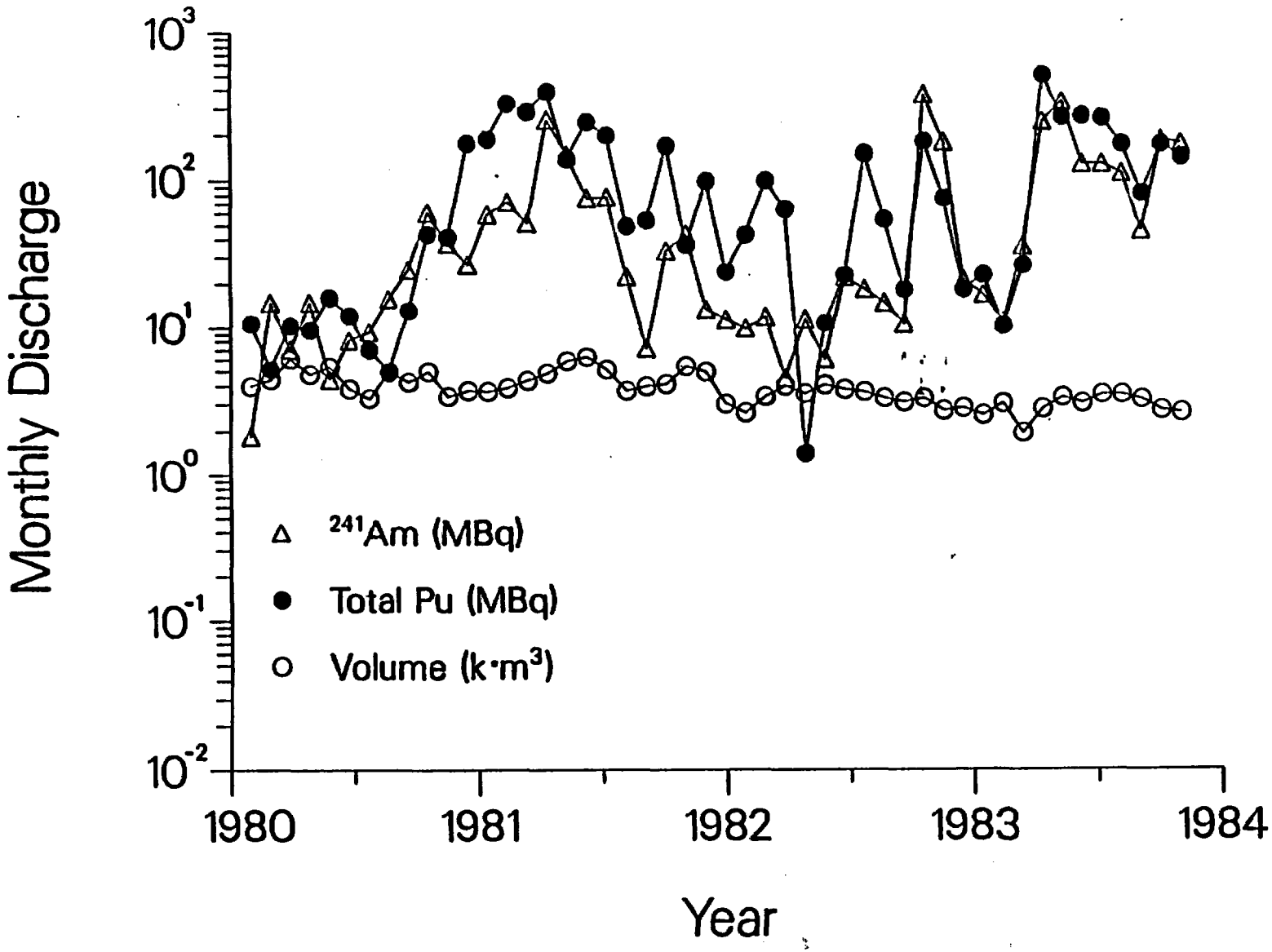
W. R. Penrose, D. M. Nelson,
and K. A. Orlandini

Liquid Waste Treatment Process at LANL

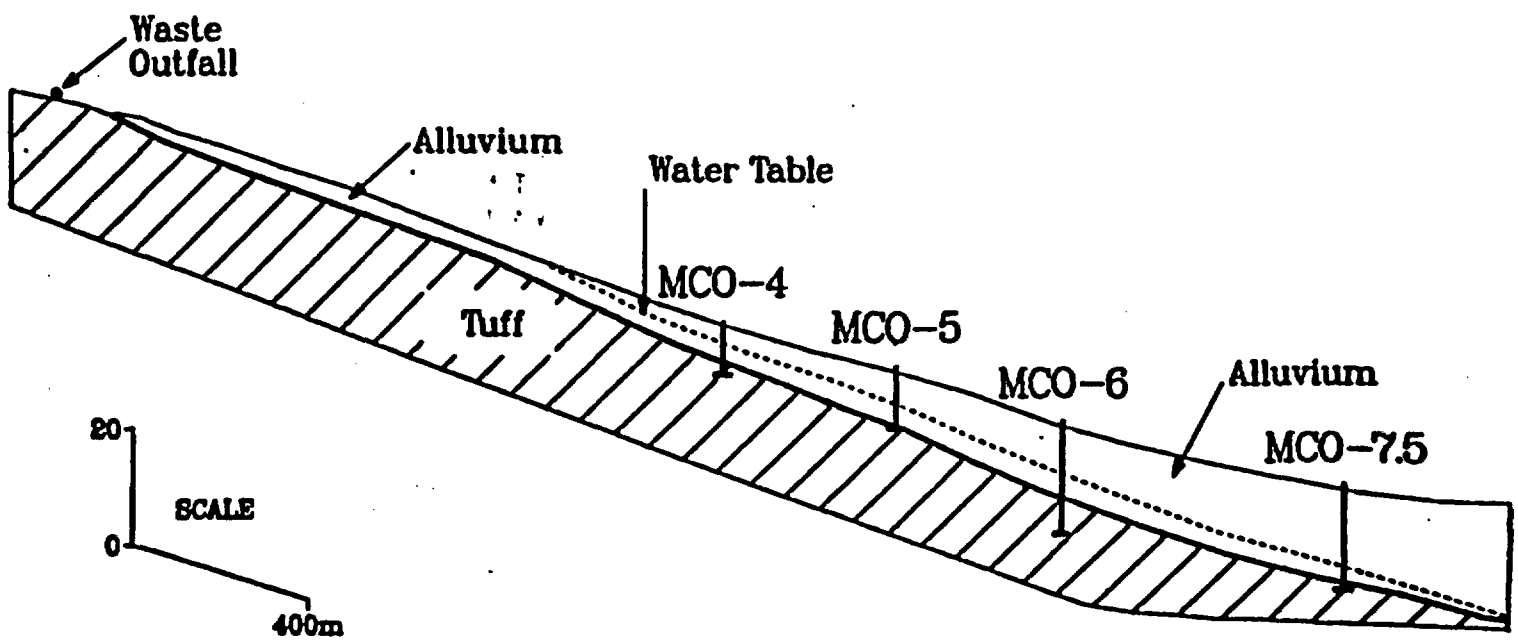
- Addition of iron sulfate and lime
- Precipitation of iron hydroxide and calcium carbonate

Treated Waste Effluent Discharge Area

- Shallow alluvium aquifer in Mortandad Canyon
- Storage capacity of aquifer
  (20-30) x 10^3 m^3
- Annual storm runoff
  (25-125) x 10^3 m^3
- Annual effluent discharge
  ~40 x 10^3 m^3
- Water movement
  ~90% subsurface


Monthly Discharge
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
^{241}Am (MBq)
Total Pu (MBq)
Volume (k·m^3)
1980
1981
1982
1983
1984
Year

Monitoring Access Wells
Mortandad Canyon Shallow Aquifer



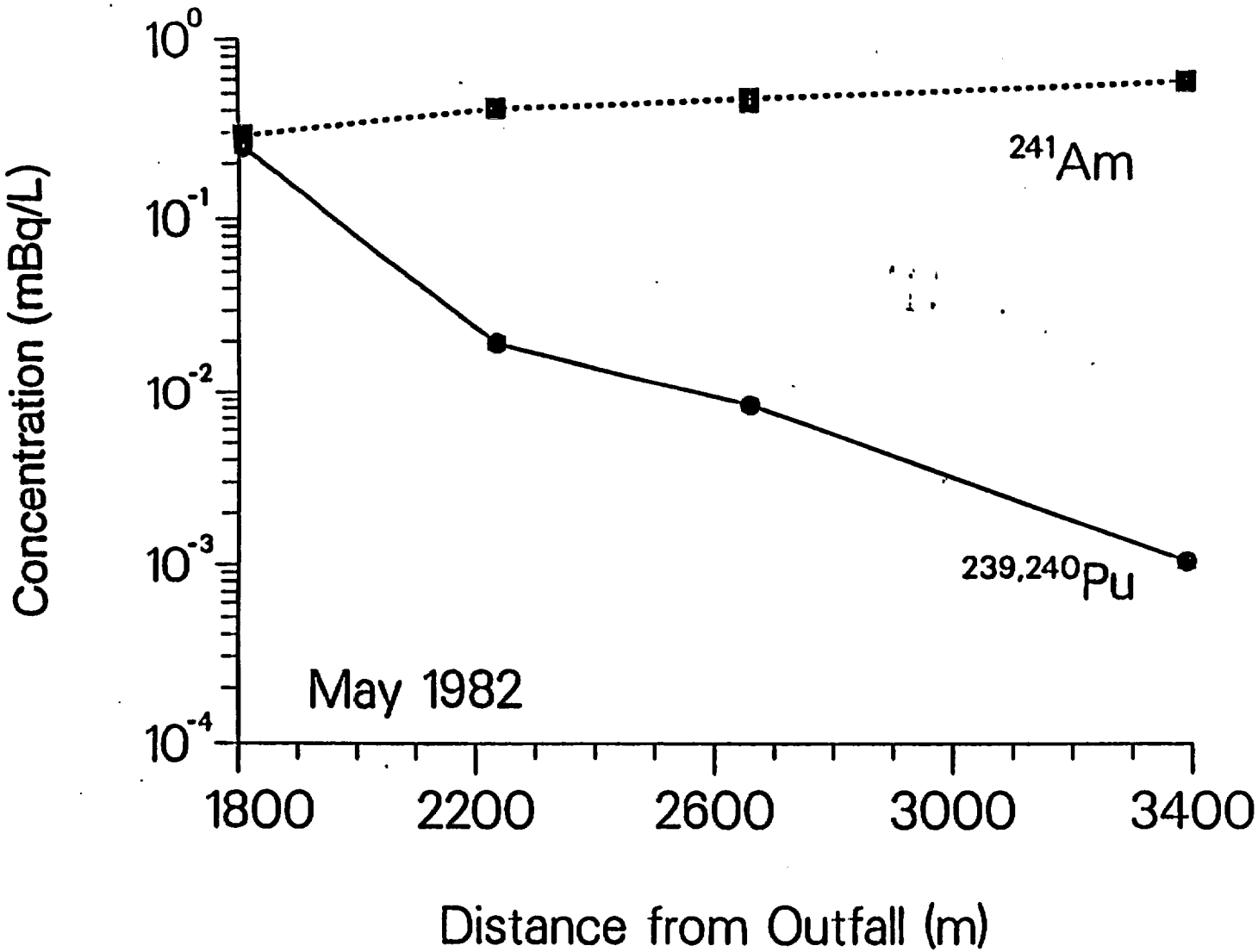
Actinide Characteristics

- Concentration
- Distribution ratio
- Oxidation state (Pu)
- Ion-exchange properties
- Size fractionation
- Chemical reactivity
- Rate of movement

Surface Sampling Station and Monitoring Wells in Mortandad Canyon (March 1983)*

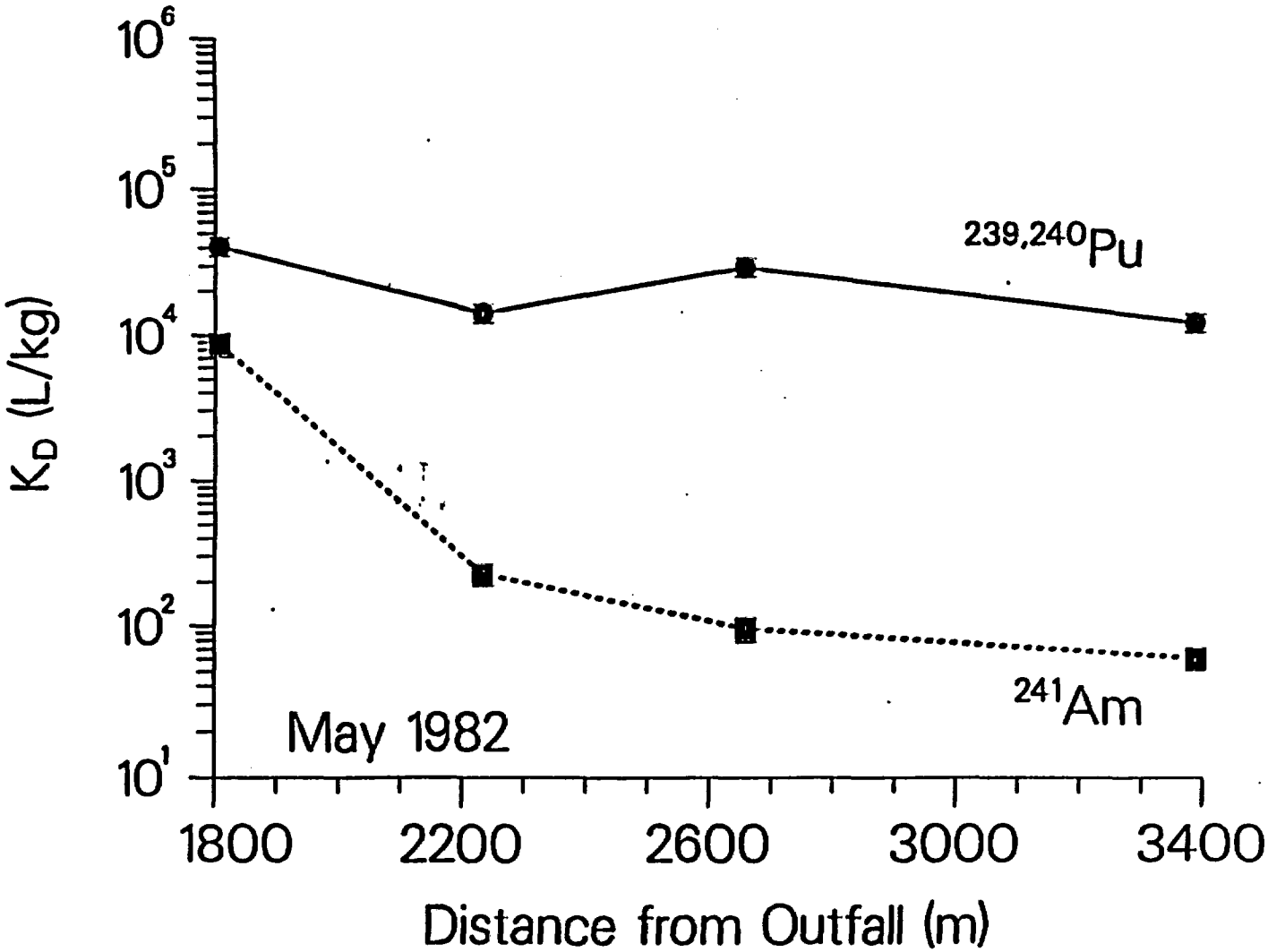
Parameter	Surface	MCO-4	MCO-5	MCO-6	MCO-7.5
Distance from outfall, m	1900	1807	2235	2660	3390
Depth of well, m		5.2	7.3	12.5	18.6
Depth to water, m		1.2	4.3	9.1	13.1
Pump depth, m		4.4	6.6	11.9	18.0
Sampling rate, L/min		4.1	2.8	3.8	1.9

*Distances are measured along the stream bed.


Concentration (mBq/L)
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
^{241}Am
^{239,240}Pu
May 1982
1800
2200
2600
3000
3400
Distance from Outfall (m)

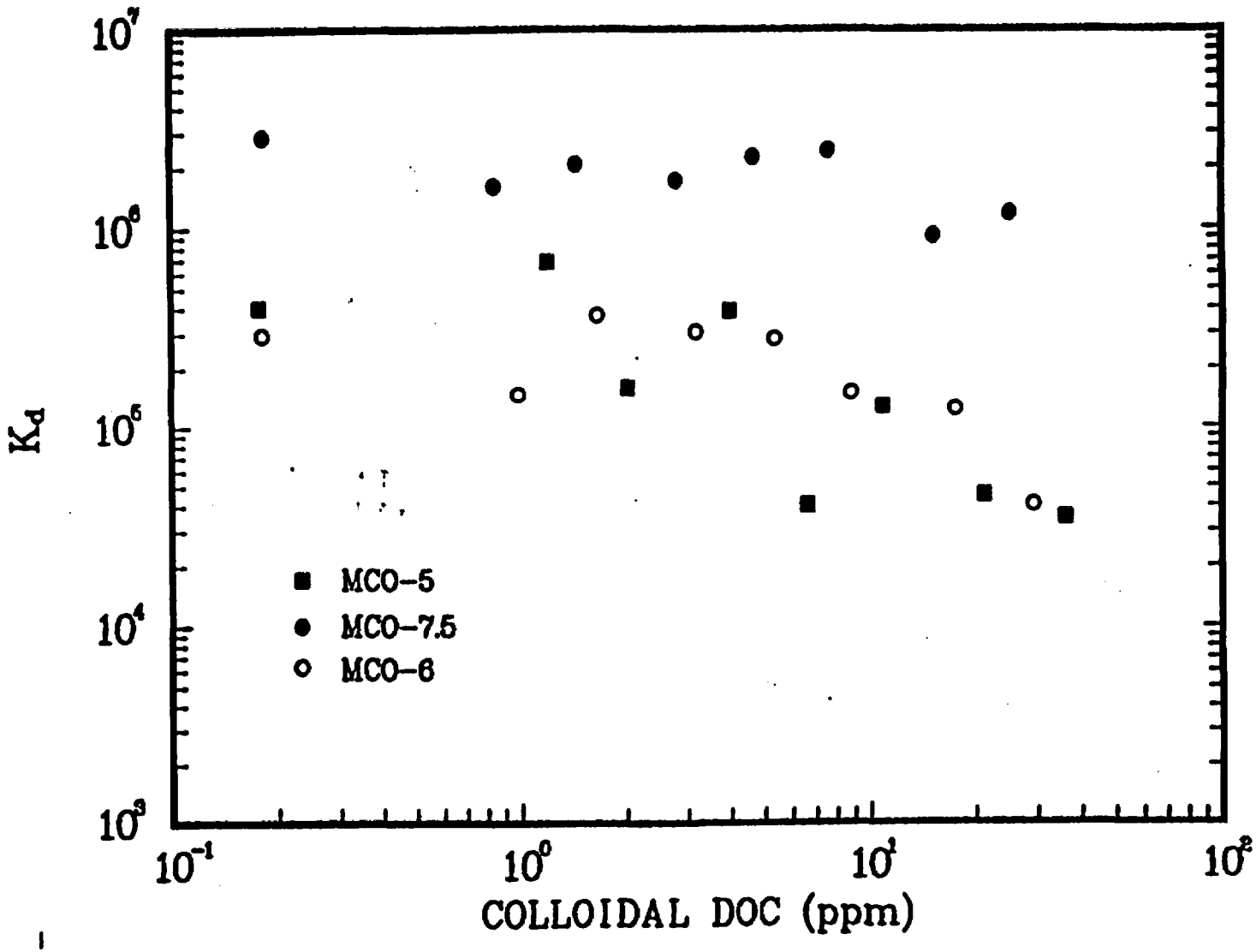
Characteristics of Aquifer Water

pH	6.4—10.1
Eh	>200 mV
O_2	>0.3 µg/mL
Oxidation state	>90% Pu[III,IV]
DOC	<22 µg/mL


10^6
10^5
10^4
10^3
10^2
10^1
K_D (L/kg)
$^{239,240}Pu$
^{241}Am
May 1982
1800
2200
2600
3000
3400
Distance from Outfall (m)

Low Molecular Weight Organics
Mortandad Canyon Aquifer

Water	Concentration (ppb)				
	Pyridenes (pyridene)	Natr'l prod (quaiacol)	Phenols (phenol)	Organ acids (isobutyric)	Alkyl benz (o-xylene)
MCO-4	2.4	24	23	140	13
Surface	1.3	14	8.4	90	9.4
MCO-5	3.7	20	28	160	17
MCO-6	2.3	19	32	110	14
MCO-7.5	3.1	16	38	94	12


10^7
10^6
10^5
10^4
10^3
K_d
MCO-5
MCO-7.5
MCO-6
10^{-1}
10^0
10^1
10^2
COLLOIDAL DOC (ppm)

Distribution of Charged Species Mortandad Canyon Aquifer

	Percent			
	$^{239,240}Pu$		^{241}Am	
Water	Anionic	Neutral	Anionic	Neutral
Waste outfall	7	94	11	78
MCO–4	2	99	3	98
Surface	3	93	3	97
MCO–5	3	96	17	84
MCO–6	4	91	46	63
MCO–7.5	8	94	31	93

Distribution of Anionic Pu Mortandad Canyon Aquifer

Water	Percent	
	^{239}Pu (ambient)	^{237}Pu (tracer)
Background	--	20
Waste outfall	7	13
MCO-4	2	29
Surface	3	--
MCO-5	3	24
MCO-6	4	--
MCO-7.5	8	56

Distribution of Anionic ^{241}Am Mortandad Canyon Aquifer

Water	Percent	
	Ambient	Tracer
Background	--	26
Waste outfall	11	6
MCO-4	3	17
Surface	3	20
MCO-5	17	18
MCO-6	46	18
MCO-7.5	31	37

Actinides in Colloidal Size Fractions Mortandad Canyon MCO–5 Water

Size fraction	Percent			
	Pu		Am	
	Ambient	Tracer	Ambient	Tracer
0.025μm–0.45μm	87	16	27	41
100K MW–0.025μm	1.0	1.0	1.0	4.0
10K MW–100K MW	5	30	11	27
<10K MW	7	52	61	28

Actinides in <100K MW Size Fractions Mortandad Canyon MCO–5 Water

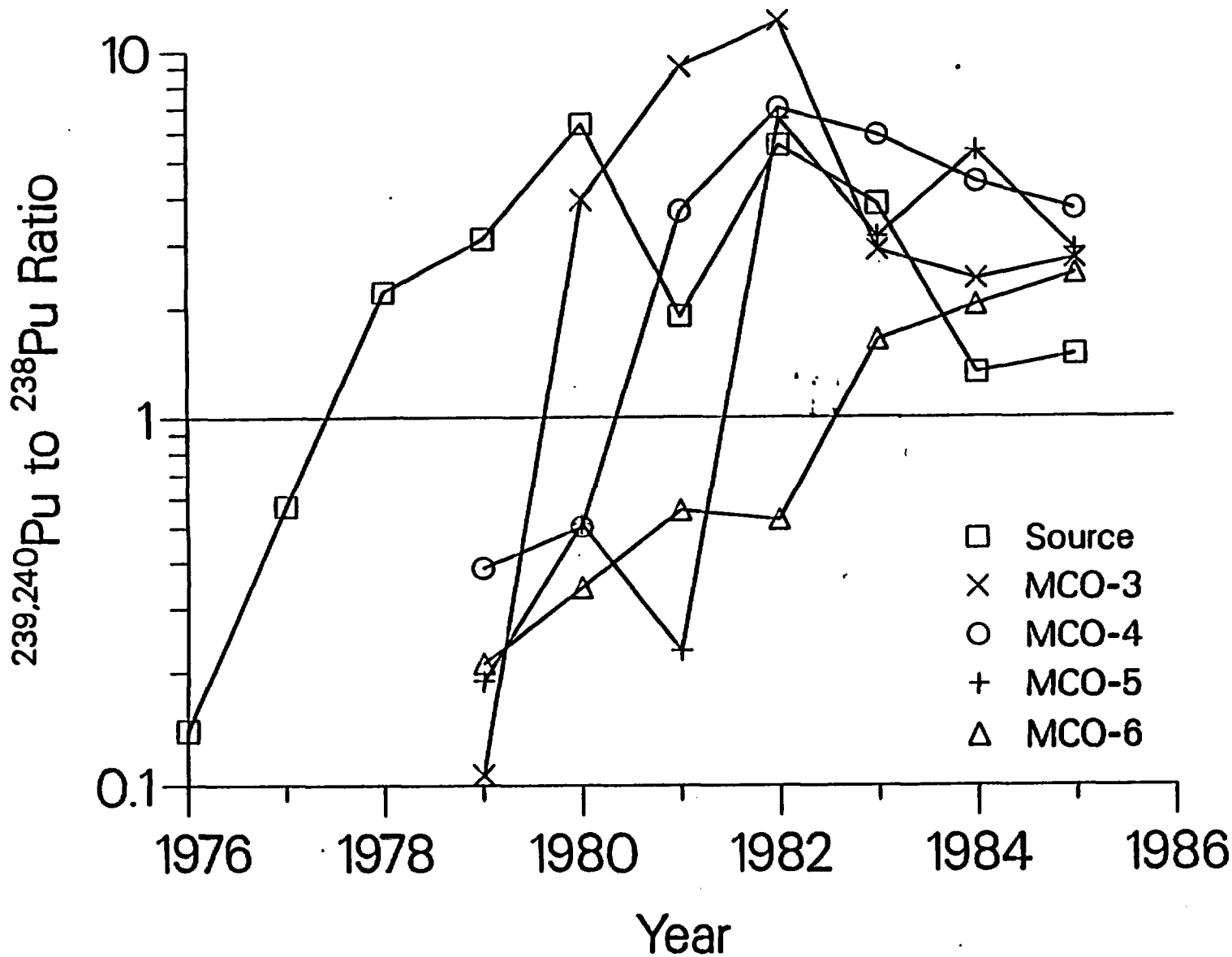
Size fraction	Percent			
	Pu		Am	
	Ambient	Tracer	Ambient	Tracer
10K MW–100K MW	43	37	15	50
<10K MW	57	63	85	50

Actinides in >10K MW Size Fractions Mortandad Canyon MCO–5 Water

Size fraction	Percent			
	Pu		Am	
	Ambient	Tracer	Ambient	Tracer
0.025μm–0.45μm	94	34	70	56
100K MW–0.025μm	0.5	2	2	6
10K MW–100K MW	5.5	64	28	38

^{238}Pu to $^{239,240}Pu$ Ratios in Mortandad Canyon Samples, - 1982 and 1983

	Distance from Outfall (m)						
	1807	1900	2235	2400	2660	3180	3390
Aquifer water 1982	0.21		0.30		0.59		5.0
Suspended sediment 1982	0.04		0.59		0.35		0.08
Aquifer water 1983	0.19		0.77		1.6		6.8
Suspended sediment 1983	0.18		0.38		0.60		0.23
Surface sediment 1983		0.15		0.16		0.25	


10
1
0.1
$^{239,240}Pu$ to ^{238}Pu Ratio
1976
1978
1980
1982
1984
1986
Year
Source
MCO-3
MCO-4
MCO-5
MCO-6

Characteristics of Actinides in Mortandad Canyon Shallow Aquifer

- Pu > 90% Pu(III,IV)

- Charge distribution
  - Predominantly neutral
  - Some negative charge

- Size distribution

  Pu —Colloidal (0.025-0.45 μm)
  Am —Colloidal (0.025-0.45 μm)
  —Soluble (<10K MW)

Characteristics of Actinides in Mortandad Canyon Shallow Aquifer (cont'd)

- Reactivity (isotopic equilibrium)
  - Irreversible—very slow to react
  - (laboratory and field)

- Rate of movement (relative)
  - Pu < water (tritium)
  - (e.g., Pu ~10 times slower than tritium)